

THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 42

MAY-JUNE, 1957

Nos. 5 and 6

SMYTHITE, A NEW IRON SULFIDE, AND ASSOCIATED PYRRHOTITE FROM INDIANA*

RICHARD C. ERD, HOWARD T. EVANS, JR., AND DONALD H. RICHTER,
U. S. Geological Survey, Washington 25, D. C.

ABSTRACT

X-ray investigation of opaque metallic inclusions in calcite crystals from Bloomington, Indiana, shows the presence of a new iron sulfide, with chemical and physical properties somewhat similar to those of pyrrhotite. This mineral is named smythite in honor of Professor C. H. Smyth, Jr. Both smythite and pyrrhotite occur as very thin hexagonal flakes, 0.05 to 2 mm. in diameter, embedded near the surface of calcite crystals found in geodes in the Harrodsburg limestone. Both are strongly ferromagnetic, and are so similar in appearance and properties that they can be distinguished with certainty only by *x*-ray tests.

Smythite is rhombohedral, space group $R\bar{3}m$ (D_{3d}^6); $a=3.47$ Å; $c=34.5$ Å; $c/a=9.94$; $G=4.06$ (obs.), 4.09 (calc.). The ideal formula, Fe_3S_4 , is derived from study of the structure by *x*-ray techniques. Many other possible structures of similar type were tested and conclusively eliminated on the basis of the Patterson function. Final hexagonal parameters are: $3Fe_1$ in (*b*); $6Fe_2$ in (*c*), $z=0.417$; $6S_1$ in (*c*), $z=0.289$; $6S_2$ in (*c*), $z=0.127$. The structure can be described as consisting of slabs of the pyrrhotite structure stacked loosely on each other in a sheet structure.

Associated pyrrhotite is the strongly ferromagnetic monoclinic phase. Study of the enclosing calcite by the visual method of inclusion thermometry indicates that pyrrhotite and smythite formed at temperatures between 25° and 40° C. and at low pressures. Synthesis of smythite by fusion or from solutions was not successful. Its origin and relationships are discussed.

INTRODUCTION

In June 1950, while making a study of the minerals of Indiana for the Indiana Geological Survey, Erd (1954) discovered what at first seemed to be minute flakes of biotite enclosed by calcite in quartz geodes of the lower Harrodsburg limestone. Study showed the flakes to have the physical properties and *x*-ray power pattern of ferromagnetic monoclinic pyrrhotite. Later, at the U. S. Geological Survey, a second *x*-ray pattern made of similar ferromagnetic material give a unique pattern which was wholly different from that of pyrrhotite. However, even if the then unknown mineral could have been completely separated from the pyrrho-

* Publication authorized by the Director, U. S. Geological Survey.

tite, there still would not have been sufficient material for a chemical or even quantitative spectrographic analysis. Therefore, the crystals were subjected to a crystal structure study which established the ideal composition as Fe_3S_4 , and elucidated its crystal chemical relationship to pyrrhotite (Erd and Evans, 1956). To know something of the conditions under which Fe_3S_4 and pyrrhotite originated, fluid inclusions in the enclosing calcite were studied by Richter, using the visual method of inclusion thermometry.

This mineral, Fe_3S_4 , is named smythite (smīth' it) in honor of Professor Charles Henry Smyth, Jr., economic geologist, petrologist, and for many years lecturer in chemical geology—one of the converging branches of geochemistry (Buddington, 1938). Professor Smyth (1911) was one of the earliest to recognize the occurrence of pyrrhotite in sedimentary rocks.

OCCURRENCE

Smythite and pyrrhotite occur chiefly as inclusions in calcite crystals in quartz geodes found near the base of the lower member of the Harrodsburg limestone, and rarely in geodes at the top of the underlying Edwardsville formation. The lower Harrodsburg limestone is a gray-green, coarsely crystalline, crinoidal limestone with thin beds of shale and siltstone. Geodes in this formation range commonly from 1 to 6 inches but may be more than 2 feet in diameter. The Edwardsville formation consists of interbedded greenish-gray siltstones and shales with geodes that are much smaller and less mineralized than those of the Harrodsburg. These formations mark the top of the Osage series of Mississippian age. The outcrop area, in southwestern Indiana, is far from any igneous rocks and there seems to be little evidence of any hydrothermal activity.

Smythite and pyrrhotite have been found at several localities in Monroe County and as far as 30 miles away near Medora in Jackson County. Pyrrhotite has so far been positively identified at two localities; smythite has been found at four; and either or both (as yet undetermined) are present at five other localities. The greatest abundance of both minerals occurring together was found in a road cut on the east side of State Route 37, two miles north of Bloomington, in the NW $\frac{1}{4}$ SW $\frac{1}{4}$ and SW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 21, T. 9 N., R. 1 W., Monroe County, and material from this locality was selected as the chief basis for this study. Smythite and pyrrhotite are also found in the abandoned Bloomington Crushed Stone Company quarry, less than a mile south of the first locality. The mineralization of the Harrodsburg in this quarry has been described by Fix (1939).

At the road cut both of the minerals occur as inclusions in calcite, although at other localities smythite or pyrrhotite or both have also been found imbedded in dolomite, barite, or rarely in quartz. Both smythite and pyrrhotite may be found within a single geode but there is a tendency for one or the other to be greatly predominant.

Much has been written concerning the origin of the quartz geodes (Fix, 1939) and the subject cannot be considered here. There is a great variety in the minerals present in the geodes, but a generalized paragenetic sequence can be given for those containing smythite and pyrrhotite. From the rim toward the center, the geodes are composed of cryptocrystalline quartz, often with pyrite or sphalerite on the outer surface; massive, dense, white quartz with black sphalerite; and euhedral doubly terminated quartz crystals. The massive and euhedral quartz, from widely separated localities, contains inclusions of anhydrite. The quartz shell of the geodes is frequently found to be fractured at its base and slightly flattened parallel to the bedding planes of the limestone. This is probably a result of the compressive force developed during intrastratal solution of the enclosing limestone. The fractures have been recemented by additional deposition of silica. Mineralization of the geodes was apparently subsequent to fracturing, for there is no evidence of shattering or distortion in crystals of the later minerals. The sequence of later deposition in the fractured quartz shell is: siderite, dolomite, and calcite of two generations (designated here as I and II) enclosing millerite, barite, smythite, pyrrhotite, and later marcasite and pyrite.

Calcite (I) is cloudy and acute scalenohedral in habit, whereas the crystals of calcite (II) are also scalenohedral, but less acute, and terminate in rhombohedral faces. Calcite (II) is generally 2 to 4 mm. thick. Traces of Mg, Fe, Mn, and Zn were detected microchemically in calcite of both generations. Calcite (II) exhibits a weak pink fluorescence and has a moderately strong yellow thermoluminescence which is most intense at about 220° C. and is extinguished just before the calcite begins to deprecipitate.

The included sulfides occur in both generations of calcite and project through, or are on, the surface of calcite (II). With the exception of millerite, they frequently outline the surface of the earlier crystal (Fig. 1). The greatest concentration of smythite, however, is just inside the surface of calcite (I) (Fig. 2). There is a tendency for the platy smythite and pyrrhotite crystals to lie with {0001} parallel to the scalenohedral faces, but there is no other apparent relationship to crystallographic directions in the calcite. Disregarding orientation, the occurrence of the inclusions in the two generations of calcite is similar to Merwin's description (1914) of marcasite and pyrite inclusions in calcite in a geode

from Missouri. The close association between pyrrhotite and calcite suggested possible chemical interaction in their coprecipitation to Smyth (1911). No smythite or pyrrhotite was found in the surrounding rock.

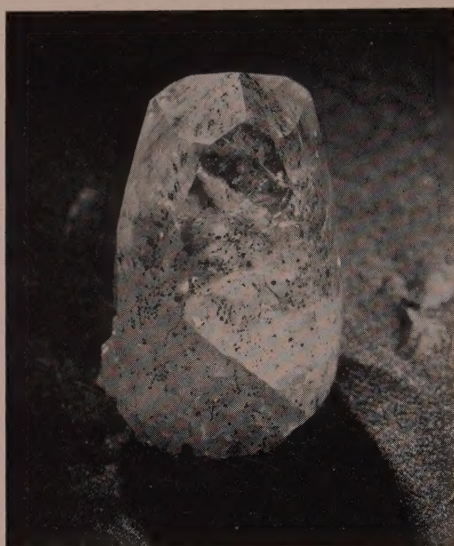


FIG. 1. Smythite inclusions in calcite crystal from the Bloomington Crushed Stone quarry. The sharper scalenohedral habit of the earlier calcite (I) can be seen outlined in phantom by the smythite near the top of the crystal.



FIG. 2. Calcite in quartz geode containing dark band of smythite inclusions indicated by S. Specimen from road cut on Indiana Highway 37, 2 miles north of Bloomington.

PROPERTIES

Physical and optical

The small size of the smythite crystals made measurement of physical properties difficult. Cleavage, which was observed only in the larger flakes, is basal and perfect. The fracture is subconchoidal to smooth. The thin laminae are flexible and elastic. Smythite is soft, being readily scratched with a steel needle. A specific gravity of 4.06 ± 0.03 was obtained by suspension in Clerici solution. Luster on a basal surface is metallic and splendent. Against a white background smythite appears jet black with a tinge of brown; if the basal plane is used as a mirror surface smythite appears light bronze yellow. To obtain the dark-gray streak, several crystals were rubbed across a streak plate with a glass rod. Smythite is strongly ferromagnetic and, since the crystals are attracted edge-on, it is inferred that the direction of easiest magnetization is within the basal plane. The similarity in magnetic properties between smythite and the associated pyrrhotite causes difficulty in obtaining a clean separation.

Optically, smythite is opaque. It seems to be free from inclusions and fresh except for some slight tarnishing and irregular small pitting. In vertically reflected light the color is pinkish cream and not perceptibly different from that of pyrrhotite. Polished prismatic sections are strongly anisotropic, with yellow and blue-gray interference colors, and strongly pleochroic from grayish yellow to reddish brown. Other than the noticeably stronger pleochroism, the optical properties of smythite are similar to those of the associated pyrrhotite.

The cleavage, flexibility, softness, and optical properties of smythite are in accord with the properties characteristic of such other layer-structure minerals as valleriite, sternbergite, covellite, molybdenite, and graphite. Nevertheless, the exceedingly thin flaky habit of the crystals makes it practically impossible to distinguish smythite from the associated pyrrhotite except by an x-ray diffraction test.

Chemical composition and behavior

There was not sufficient material available for quantitative analysis, even by microtechniques, but qualitative microchemical tests showed the major constituents to be iron and sulfur with a minor amount of nickel and traces of copper and zinc. Spindles of smythite and pyrrhotite from Bloomington were examined by means of a curved-crystal x-ray fluorescence spectrometer which showed iron and a small amount of nickel to be present. As the samples were not run against a calibrated standard, the exact atomic ratios are not known with certainty, but smythite seems to contain about half as much nickel as that present in pyr-

rhodite, which is probably less than 1 per cent. Copper and zinc were not detected by this method.

Smythite seems to be more resistant to chemical attack than pyrrhotite. It is slowly soluble in cold dilute hydrochloric or nitric acid and in solutions of potassium hydroxide or silver nitrate. It is very slowly soluble in cold dilute sulfuric acid and is not attacked by carbon disulfide. Smythite left in contact with distilled water was tarnished and pitted after one week, whereas pyrrhotite was attacked to the same extent after three days. Smythite quickly decomposes in a strong (30%) solution of hydrogen peroxide leaving a residue of iron oxide.

When strongly heated, in either a closed or open tube, flakes of smythite warp, curl, and split as they are oxidized to hematite. Smythite remained unchanged when heated in a sealed evacuated tube at 200° C. for one month, but when heated in the enclosing calcite to 400° C. for 18 hours smythite changed completely to pyrrhotite and possibly pyrite although lines of the latter could not be detected in the powder pattern. The pattern was too poor, to determine whether the monoclinic or hexagonal modification of pyrrhotite was formed. The reaction is irreversible. The temperature at which this dissociation begins has not been exactly determined, but a powder pattern of smythite heated in calcite to approximately 290° C. for 18 hours shows diffraction lines of both pyrrhotite and smythite. Some of the smythite crystals, partly exposed by decrepitation of the calcite, oxidized to magnetite, which is evidently the first product of oxidation. In the normal weathering environment smythite alters to goethite. It is only preserved within calcite, dolomite, and none was found in the enclosing rock.

Syntheses and analyses of iron sulfides related to Fe_3S_4

It is of interest that Sidot (1868) claimed to have synthesized ferrosic sulfide (Fe_3S_4) by the reaction of magnetite and hydrogen sulfide at red heat. Attempts made (de Jong and Willems, 1927; Fontana, 1927; Juza, Biltz, and Meisel, 1932; and Michel, 1937) to repeat Sidot's reputed synthesis or otherwise to synthesize Fe_3S_4 with spinel structure, analogous to linnaeite (Co_3S_4), violarite (FeNi_2S_4), and polydymite (Ni_3S_4), apparently were unsuccessful, and most of these workers agreed that the existence of ferrosic sulfide with spinel structure is unlikely. Michel (1955, 1956) has recently made a comprehensive study of the reaction between hydrogen sulfide and iron oxides, and reports only FeS as forming in these reactions.

Iron sulfides, or alkali iron sulfides, and their hydrates, with x-ray patterns differing from those of the common iron sulfides, have been prepared from water solutions at ordinary temperatures by Alsen (1923),

Lepp (1954), and Rosenthal (1956), but, so far as we know, none of these compounds gave the powder pattern of smythite. Stevens (1933) prepared similar compounds but gave no x-ray data. Lundqvist (1947) synthesized Ni_3S_4 with spinel structure from a water solution, but only repeated and confirmed the work of Allen *et al.* (1912) with the iron sulfides.

Our efforts to synthesize Fe_3S_4 , either by fusion or from water solutions, have not been successful; however a systematic program was not attempted. Three different black ferromagnetic compounds, all poorly crystallized as indicated by the diffuse powder diffraction lines, have been obtained from water solutions at room temperature but none shows any relation to smythite. All of these compounds are rapidly attacked by hydrogen peroxide. The common association of pyrrhotite with calcite, in its low-temperature occurrences, suggests the use of calcite to reproduce environmental conditions and also as a surface for nucleation in the synthesis of pyrrhotite or smythite. Weil (1955) emphasized the importance of calcite in his synthetic reproduction of the sulfides found in sediments. Following the directions of Rodgers (1940) for the use of Lemberg's black stain for calcite, but substituting Na_2S for $(\text{NH}_4)_2\text{S}_x$, we obtained an unidentified product, which also is unrelated to smythite. Powder-diffraction data and details of our experiments are given in the Appendix.

Several analyses reported for pyrrhotite reach, or even exceed, the theoretical 57.14 atomic per cent sulfur in smythite, namely those of Stromeyer (1814) 57.43%, Meunier (1869) 55.79%, and Schulze (reported by Stelzner, 1896) 55.46%. These investigations pre-dated x-ray analysis, but the descriptions of the various materials analyzed would indicate that none of the analyses was of smythite. Pyrrhotite from Ertelien, Norway and Petsamo, U.S.S.R., with 56.7 and 55.2 atomic percentages of S, respectively, are regarded by Pehrman (1954) as representing the analysis of material incompletely separated from pyrite or chalcopyrite. He reports three pyrrhotites from Finland as having 54.6, 54.4, and 54.0 atomic per cent S; all exhibited only the monoclinic modification of pyrrhotite in their powder patterns.

Eakle (1922) suggested Fe_3S_4 as the pyrrhotite end member, and Lipin (1946) considered pyrrhotite to be a solid solution of Fe with Fe_2S_3 or Fe_3S_4 . However Hägg and Sucksdorff (1933) found the value represented by Fe_4S_5 (55.5 atomic per cent S) as the sulfur-rich composition limit for the pyrrhotite structure. Grønvold and Haraldsen (1952) thought that this value was too high, and that, for temperatures up to 360° C., the limit of the deficiency of iron is close to the composition Fe_7S_8 (53.27 atomic per cent S).

We suggest that smythite represents a stable phase in the Fe-S system, which forms at low temperature and pressure, and which dissociates into pyrrhotite and pyrite or sulfur at a temperature between 200° and 290° C. It is likely that it would occur only in sedimentary rocks or in epithermal deposits.

CRYSTALLOGRAPHY

Morphology

Crystals of smythite range from 0.05 to 1.25 mm. in diameter (most are 0.10 to 0.25 mm. in diameter) and are 1 to 3 microns in thickness. Subhedral irregularly formed crystals are uncommon; most are euhedral platy hexagonal crystals which appear to be a combination of a well-developed base {0001} and a rhombohedron. The prism face was not observed. Even some of these apparently simple crystals, however, were found by x-ray study to be twinned on (0001). About half of the crystals are aggregates of intersecting plates. In some, repeated twinning has produced hexagonal plates which have the appearance of being warped.

X-ray powder data

X-ray powder data for smythite and pyrrhotite from Bloomington, Indiana, are given in Table 1. The data for the latter is identical to a pattern of pyrrhotite from Lairdsville, New York, collected by Professor Smyth (Princeton Collections no. 16/74). The smythite pattern was indexed on the values for c and a obtained from the single-crystal study.

Crystal structure and crystal chemistry

A crystal-structure study was made to ascertain the chemical constitution of smythite because of the impracticability of obtaining sufficient material for a chemical analysis. By this means it was possible to establish the chemical formula conclusively as Fe_3S_4 , and to elucidate its structural relationship to pyrrhotite.

Buerger precession photographs of the ($hk.0$), ($h0.l$), and ($hh.l$) net planes established the lattice as rhombohedral, with the following cell constants:

Space group: $R\bar{3}m(D_{3d}^5)$, $R3m(C_{3v}^5)$, or $R32(D_3^7)$.

Cell dimensions:

rhombohedral: $a = 11.66 \pm 0.03 \text{ \AA}$, $\alpha = 17^\circ 7' \pm 30'$

hexagonal: $a = 3.47 \pm 0.02 \text{ \AA}$, $c = 34.5 \pm 0.2 \text{ \AA}$

Cell volume (hex.): $360 \pm 3 \text{ \AA}^3$

Cell contents (hex.): $3[\text{Fe}_3\text{S}_4]$

Specific gravity: 4.09 ± 0.04 (calc.); $4.06 \pm .03$ (meas.).

A close relationship to pyrrhotite is apparent when the cell constants are compared: β -pyrrhotite (ignoring superstructures) has the (pseudo)

space group $C6_3/mmc$, with $a=3.44$ Å and $c=5.70$ Å ($6c=34.2$ Å). The specific gravity of pyrrhotite (Fe_7S_8) is 4.62. The symmetry and dimensions of smythite place close restrictions on the arrangement of Fe and S atoms in the unit cell. The atoms must all lie on the three 3-fold axes in the cell, but in an identical manner on all three, instead of all Fe on one and all S on the other two as in pyrrhotite. On the basis of these facts, a tentative structure was worked out, keeping in mind the close similarity of smythite and pyrrhotite in nearly all physical and chemical properties.

In Fig. 3, projections are shown of the simple structure of pyrrhotite

TABLE 1. X-RAY POWDER DATA FOR SMYTHITE AND PYRRHOTITE FROM BLOOMINGTON, INDIANA

FeK α radiation; 114.6 mm. dia. camera; d (obs.) cut-off at 16.0 Å

A. SMYTHITE

hkl	d (calc.)	d (obs.)	I	hkl	d (calc.)	d (obs.)	I
00.3	11.50	11.5	6	11.12	1.486		
00.6	5.75	5.75	0.5	02.4	1.481		
00.9	3.83	3.82	2	20.5	1.468	1.465	0.5
10.1	2.99	3.00	6	00.24	1.437	1.435	2
01.2	2.96	2.96	0.5	02.7	1.437		
00.12	2.87	2.86	0.5	20.8	1.418	1.427	6
10.4	2.84	2.83	2	02.10	1.377	1.375	0.5
01.5	2.75	2.75	4	20.11	1.354	1.351	0.5
10.7	2.56	2.56	6	01.23	1.342	1.332	0.5
01.8	2.46	2.45	2	02.13	1.308	1.305	2
00.15	2.30	2.29	0.5	11.18	1.286		
10.10	2.26	2.26	6	20.14	1.283	1.280	2
01.11	2.17	2.16	4	00.27	1.279		
10.13	1.988	1.979	7	10.25	1.254	1.254	0.5
00.18	1.917			20.17	1.207	1.204	2
01.14	1.903	1.897	8	02.19	1.158	1.154	0.5
10.16	1.751			00.30	1.150		
11.0	1.736	1.732	10	11.24	1.107		
11.3	1.715	1.715	0.5	01.29	1.105	1.102	4
01.17	1.681	1.687	0.5	02.22	1.084	1.078	0.5
11.6	1.662	1.672	4	20.23	1.061	1.065	0.5
00.21	1.642			00.33	1.045		
11.9	1.581	1.577	0.5	10.31	1.043	1.037	2
10.19	1.554	1.546	0.5	11.27	1.029	1.029	0.5
02.1	1.500			30.0	1.001	1.001	2
20.2	1.497	1.496	0.5	30.3	0.997	0.998	2
01.20	1.496			20.26	0.995		
				30.6	0.987	0.988	0.5

(Continued on next page)

B. PYRRHOTITE

Note: Calculated lines correspond to hexagonal pseudo-cell; other lines correspond to monoclinic superlattice of β -pyrrhotite.

<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i>	<i>hkl</i>	<i>d</i> (calc.)	<i>d</i> (obs.)	<i>I</i>
		5.75	4	20.0	1.49	1.488	0.5
		5.29	2	11.2	1.47		
		4.72	2	20.1	1.44	1.439	2
10.0	2.97	2.97	8	00.4	1.42	1.424	6
00.2	2.84	2.84	4	20.2	1.32	1.320	4
		2.70	0.5	10.4	1.28	1.286	0.5
10.1	2.64	2.64	9			1.230	0.5
		2.27	4	20.3	1.17	1.174	0.5
		2.21	2			1.138	0.5
		2.16	2			1.105	0.5
10.2	2.06	2.06	10	11.4	1.095	1.100	4
		2.01	0.5			1.065	0.5
		1.946	0.5	21.2	1.045	1.049	2
		1.914	0.5			1.043	4
11.0	1.72	1.717	8	30.0	.991	0.992	6
		1.632	0.5				
10.3	1.60	1.606	2				

along the *c* and *a* axes. Also shown is the smythite structure as it was finally deduced, projected along the *a* axis. With reference to this figure, the following description of the solution of the structure may be more clearly understood.

Starting at the origin (symmetry center) of the rhombohedrally centered hexagonal cell, a model structure was developed by building a pyrrhotite structure upward until symmetry restrictions interfered. Thus, the smythite cell was found able to accommodate a pyrrhotite structure four sulfur and three iron layers deep, but beyond this point, a shift in the structure is required because of the rhombohedral lattice node at $\frac{2}{3}\frac{1}{3}\frac{1}{3}$. Starting anew at this point, a second slab of pyrrhotite structure was erected until the point $\frac{1}{3}\frac{2}{3}\frac{2}{3}$ was reached, where another shift is required. In this way, the pyrrhotite structure was found to fit the smythite unit cell, but with shifts in the structure after each fourth layer of sulfur atoms along the *c* direction. The best way to account for these shifts seemed to be to assume that the iron atoms that would be coordinated between the shifted sulfur layers are actually omitted, thus giving rise to a layer structure consisting of pyrrhotite slabs loosely stacked on each other in a rhombohedral mode. This hypothesis led directly to the formula Fe_3S_4 , which was subsequently confirmed by density measurement. The symmetry of the proposed structure was then

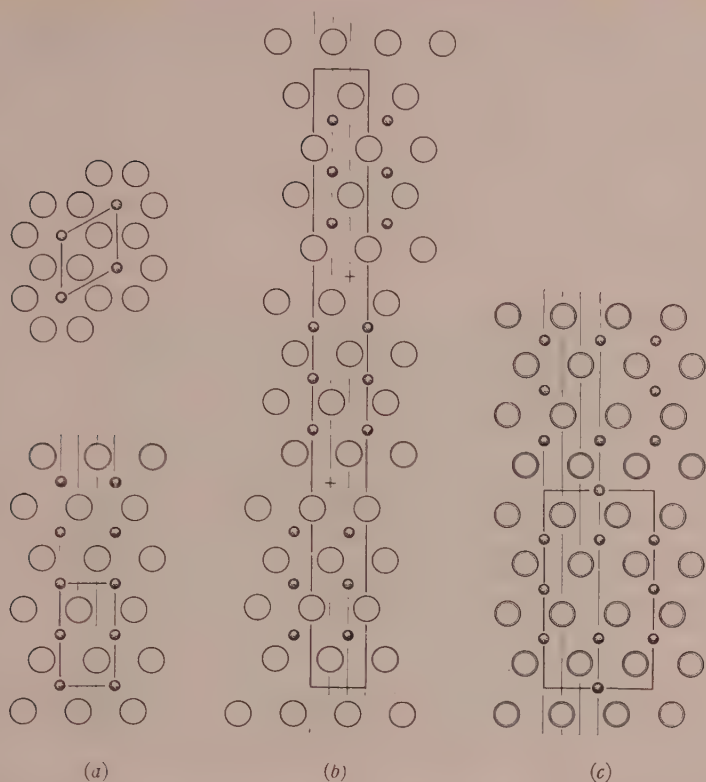


FIG. 3. Crystal structures of smythite and related structures. (a) Pyrrhotite structure projected along hexagonal c axis (top) and a axis (bottom). (b) Smythite structure projected along hexagonal a axis. (c) Fe_3Se_4 structure projected along pseudohexagonal a axis. Fe atoms represented by small shaded circles, S atoms by large single circles, Se atoms by large double circles. Three-fold axes represented by vertical lines.

assumed to be $R\bar{3}m$, and coordinates assigned to the atoms as follows: 3Fe_1 in (b) with $z = \frac{1}{2}$; 6Fe_2 in (c) with $z = 5/12$; 6S_1 in (c) with $z = 7/24$; 6S_2 in (c) with $z = 3/24$.

To test this structure, intensities were measured for 35 ($h0l$) reflections, using the Buerger precession photograph shown in Fig. 4. It is apparent from this pattern that the intensities could not be measured to the usual standards of accuracy, since the photograph shown is the best that could be obtained from the available crystals. Intensities were estimated by comparison with a calibrated series of spots made from another crystal. The intensities were multiplied by a correction factor of the form $(w+r\tau)/w$ in an attempt to counteract the smearing effect on the spots resulting from the angular distortion of the crystal which is

apparent from the photograph. In this expression, w represents the normal spot diameter, r the distance of the spot from the center of the pattern, and τ the angle of distortion in radians. The Lorentz-polarization correction was estimated by means of a Waser chart (Waser, 1951). No correction was made for absorption. The crystal was approximately 0.2 mm. across and 5 microns thick, and required 72 hours exposure, using unfiltered MoK radiation at 50 kv and 20 ma to give the pattern shown.

The first trial of the hypothetical structure gave a reliability factor of

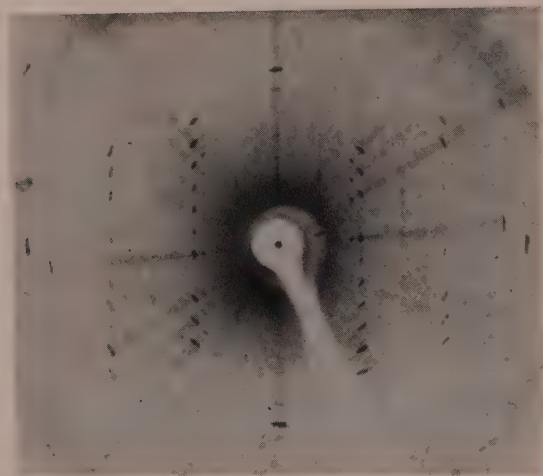


FIG. 4. Buerger precession photograph of $(h0l)$ net plane of smytheite. MoK radiation, unfiltered.

20.5%, which was taken as strong evidence of the correctness of the structure. Nevertheless, it was recognized that many other structures could be postulated which satisfy the structural restrictions referred to earlier, plus other requirements that can be defined. Allowing both octahedral and prismatic coordination for iron (the latter being exemplified by molybdenum in MoS_2), it was found that 25 different model layer structures could be built which would fit the unit cell with space group $R\bar{3}m$ or $R3m$. The Patterson function $P(0,z)$ was evolved for each of these and compared with the Patterson function calculated from the observed intensities. A good match was found for only one of the 25 structures, the one corresponding to that already described. Reliability factors calculated for some of these structures ranged from 30 to 45%. It seems unnecessary to consider any structures further, aside from the one described.

The postulated structure was refined by least squares analysis (using

unweighted values of ΔF), giving final parameters listed below:

Space group: $R\bar{3}m(D_{3d}^5)$

Parameters:

3Fe_1 in (b) , $(z=\frac{1}{2})$

6Fe_2 in (c) , $z=0.4171\pm0.0006$

6S_1 in (c) , $z=0.2888\pm0.0010$

6S_2 in (c) , $z=0.1270\pm0.0010$

This structure, with a temperature factor e^{-Bs^2} applied to the calculated

TABLE 2. COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS OF SMYTHITE

$h0.l$	$F(\text{calc.})$	$F(\text{obs.})$	$h0.l$	$F(\text{calc.})$	$F(\text{obs.})$	$h0.l$	$F(\text{calc.})$	$F(\text{obs.})$
00.30	-48	A	10.28	-3	A	20.17	83	97
00.27	-51	51	10.25	-58	41	20.14	108	120
00.24	197	201	10.22	43	58	20.11	-108	74
00.21	-28	51	10.19	-48	62	20.8	26	53
00.18	-31	32	10.16	17	44	20.5	-45	48
00.15	-43	44	10.13	-167	152	20.2	38	34
00.12	42	46	10.10	145	120	20.1	-86	81
00.9	-59	53	10.7	143	118	20.4	-19	34
00.6	-76	N	10.4	-28	32	20.7	103	92
00.3	-78	N	10.1	-126	118	20.10	104	79
00.0	426	—	10.2	57	55	20.13	-122	109
			10.5	-64	84	20.16	13	A
			10.8	35	77			
			10.11	-151	120			
			10.14	145	159			
			10.17	105	106			
			10.20	-40	A			
			10.23	-91	55			
			10.26	28	A			
			10.29	-33	44			

N=not measured

A=absent

$R=0.186$

$B=0.90\pm0.3 \text{ \AA}^2$

structure amplitudes in which $s=(\sin \theta)/\lambda$ and $B=0.90 \text{ \AA}^2$, gives a reliability factor of 18.5%. No significance can be attached to the value of B , since it depends in large measure on the choice of w and τ used in the expression applied to correct intensities for pattern distortion as described above. Final calculated and observed structure factors are listed in Table 2.

A Fourier synthesis of the electron density in smythite along one three-fold axis was carried out by means of the function

$$= \frac{1}{A} \sum F(h0.l) \cos 2\pi lz$$

and the result is shown on a relative scale in Fig. 5. A synthesis is also shown in which the values of F in the series are replaced by ΔF . The peaks correspond well with the postulated atomic positions, and there are no features that justify special interpretation.

The structure is entirely consistent with the normal pyrrhotite structure, except for the layer feature. This consistency is demonstrated by

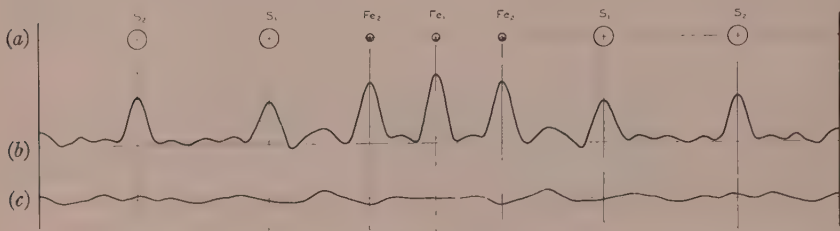


FIG. 5. Fourier synthesis of electron density in smythite. (a) Position of atoms on one three-fold axis. (b) Electron density on arbitrary scale along the three-fold axis. (c) Electron density residual along the three-fold axis on same scale as (b).

the interatomic distances given in Table 3 and Fig. 6. Standard deviations shown in the table were computed from the standard deviation of the structure amplitudes. Evidently, the structure itself calls for no special comment.

Two further observations on the crystallography of smythite may be noted. First, there is evidence on the photograph of Fig. 4 of twinning on (00.1). Such twinning is to be expected from an uncertainty in the direction of rhombohedral stacking resulting from the very slight energy difference that must obtain between rhombohedral and hexagonal stacking of the layers. Second, there is evidence on the photograph of a superlattice based on the rhombohedral lattice described, which is also probably rhombohedral but with the a axis and possibly the c axis doubled. There is no way in which variations in the stacking sequence of the layers could double the a axis; therefore, there is a strong possibility that the superstructure results from the ordering of vacancies resulting from a small deficiency of iron, as in the case of β -pyrrhotite.

It is of interest to compare the structure found for Fe_3S_4 with that recently proposed for a new synthetic compound, Fe_3Se_4 , described by Okazaki and Hirakawa (1955). According to these authors, Fe_3Se_4 is monoclinic with space group $P2/m(C_{2h}^1)$, $a = 6.167 \text{ \AA}$, $b = 3.517$, $c = 11.7$ and $\beta = 92.0^\circ$. The structure is described as being directly derived from a distorted pyrrhotite structure with one out of every four Fe atoms absent. The atoms are arranged in the unit cell described with 1 Fe in (e)

at $\frac{1}{2}\frac{1}{2}0$; 1 Fe in (c) at $00\frac{1}{2}$; 2 Fe in (l) at $\frac{1}{2}\frac{1}{4}\frac{1}{2}$, $\frac{1}{2}\frac{3}{4}\frac{1}{2}$; 2 Fe in (i) at $0\frac{1}{4}0$, $0\frac{3}{4}0$; and vacancies at the sites (a) at 000, and (h) at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. As shown in Fig. 3c, this arrangement leads to rows of three Fe atoms along the *c* axis, but they are staggered with respect to each other in the hexagonal close-packed sulfur framework, and consequently a layer structure does not result as in smythite.

TABLE 3. INTERATOMIC DISTANCES IN SMYTHITE

(See Fig. 6)

Vector	Atoms	Smythite	Other structures
A	Fe ₁ to Fe ₂	$2.86 \pm 0.02 \text{ \AA}$	2.84 \AA (pyrrhotite)
B	Fe ₁ to S ₂	2.42 ± 0.04	2.44 (pyrrhotite)
C	Fe ₂ to S ₂	2.50 ± 0.04	
D	Fe ₂ to S ₁	2.42 ± 0.04	
E	S ₂ to S ₂	3.39 ± 0.05	3.46 (pyrrhotite)
F	S ₁ to S ₂	3.48 ± 0.05	
G	S ₁ to S ₁	3.67 ± 0.05	3.67 (molybdenite)
H	Fe ₂ to S ₂	4.43 ± 0.07	
J	S-S (<i>a</i> axis)	3.47 ± 0.01	3.44 (pyrrhotite)

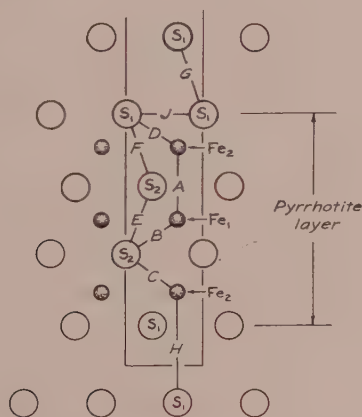


FIG. 6. Atom types and interatomic vectors in smythite.

CONDITIONS OF FORMATION AS INDICATED BY FLUID INCLUSIONS

It is clear that smythite and pyrrhotite were formed at the same time and under the same pressure and temperature conditions as the enclosing calcite. Fluid inclusions in coarsely crystalline transparent calcite, containing smythite, from two widely separated localities were investigated by the visual (Sorby) method of inclusion thermometry. More than 200

fluid inclusions were studied in six polished thick sections and numerous thin cleavage plates.

Two distinct types of fluid inclusions, based on physical appearance and orientation, were observed in the calcite. Inclusions of type 1 are flat, usually with an irregular outline and probably occur on the $\{10\bar{1}1\}$ planes. Some are in the form of complex or multiple parallelepipeds with the acute plane angles approximately those of the cleavage rhombohedron of calcite, viz. 75° . The inclusions range in size from less than 0.02 mm. to 0.10 mm., the smaller being more abundant. Type 2 are very small (<0.002 mm.) tubular and ovoid-shaped inclusions occurring in short gently curving and intersecting planes; hundreds are present in one minute plane.

The inclusions, whether of type 1 or 2, are all one-phase at room temperature. When heated to temperatures above 225°C ., and then cooled, a large amount of vapor phase is formed due to leakage of liquid along fractures or parted cleavage plates. With a linear heating rate of approximately 20°C./minute the calcite decrepitates at 265°C . Furthermore, when cooled with liquid nitrogen the calcite also fractures, due in this case to the expansion and relative incompressibility of the solid phase formed. The inclusion fluid, therefore, is undoubtedly liquid. Attempts to separate a vapor phase in the inclusions by cooling to 1°C ., in a microscope-mounted ice bath, were unsuccessful in all but four of the larger type-1 inclusions. Assuming that pressure-temperature conditions in the inclusion were the same as those in the growth solution, and the interfacial tension was negligible, a vapor phase should form on cooling prior to the temperature of maximum density, unless, of course, the calcite formed at that temperature (4°C .). However, inasmuch as the volume change is only -0.60% when cooled from 35°C . to 4°C . (the temperature of maximum density of pure water), it is very possible that the interfacial tension between inclusion fluid and calcite is strong enough to prevent contraction of the liquid and the formation of a vapor phase. This is further substantiated by the fact that only the larger inclusions, which have a relatively small surface area per unit volume, become two-phase on cooling below room temperature.

After removal from the cooling chamber, the four larger inclusions, in which a vapor phase was formed, completely filled with liquid at temperatures of 27, 31, 35, and 38°C . The three higher filling temperatures were determined in a microscope-mounted heating chamber. It is probably safe to assume, therefore, that all the inclusions, especially those of type 1, would have filling temperatures somewhere within this range if the liquid on cooling had formed a vapor phase.

The determination of formation temperatures of minerals from fluid

inclusion studies are based on a number of important assumptions. Although these assumptions, which were made in part by Sorby (1858) in his classical work, have been considered in detail in recent years by many workers (Ingerson, 1947; Bailey and Cameron, 1951; Cameron, Rowe, and Weis, 1953; and Smith, 1953), it is necessary in each individual investigation to review the assumptions, in order to evaluate fully all experimental and other data. Although all assumptions, which are discussed below, cannot be rigorously proved to be correct, they do allow very probable geothermometric conclusions.

- (1) The inclusions were completely filled with liquid at the time of formation and have not lost or gained liquid since that time.

The solutions responsible for the deposition of calcite and associated minerals in the geodes were without much doubt aqueous, and, as evidenced by the degree of filling of the inclusions, probably completely filled the inclusions at the time of entrapment. Skinner (1953) after an investigation of fluid inclusions in quartz, concluded that high-pressure differentials between inclusion fluids and host-crystal media can force liquid into, or out of, fluid inclusions, probably along lineage boundaries. In their reply to Skinner's paper, Richter and Ingerson (1954) showed that liquid could not be forced out of primary fluid inclusions (other than leakage along fractures) in quartz and calcite under the conditions cited by Skinner. They contended, therefore, that the single crystal of quartz studied by Skinner is exceptional in some of its properties and further work is necessary before this basic assumption is invalidated. There is no evidence to suggest that liquids have migrated from the inclusions, and furthermore, consideration of concordant geological evidence of a low temperature-pressure environment, makes it seem doubtful if pressure differentials ever existed that could force liquid into the inclusions.

- (2) The inclusions contain an aqueous solution with negligible amounts of CO_2 or other gases.

The inclusion liquid, in the inclusions where a vapor phase was observed, has a low viscosity and exhibits Brownian movement. The single vapor phase when cooled to 1°C . does not separate any additional phases, nor on heating above 31°C . is there a marked increase in the size of the vapor bubble, as would be expected if significant amounts of CO_2 were present. Unfortunately attempts to determine the freezing point of the liquid were unsuccessful. It is inferred, by analogy with other analyzed inclusion fluids, and admittedly there are only a few, that the liquid is a dilute aqueous solution (5–10%) of K, Na, and Ca salts. Specimens were

crushed and leached with distilled water, but the concentration of Cl^- or SO_4^{-2} ions was too low to be detected by this method.

(3) The volume of the inclusion has remained constant.

The solubility of the calcite in the inclusion fluid at temperatures in the range of 0–35° C. and pressures up to 100 atmospheres is probably negligible. A 0.5 M NaCl solution at 24° C. under a CO_2 pressure of 50 bars dissolves less than 1% of calcite (Miller, 1952). At considerably lower, or zero, CO_2 pressures, which would be comparable to the system under investigation, the solubility would be much less.

At temperatures and pressures in the range given above, the compressibility of water is more than 30 times that of calcite (Birch, 1942), and therefore a change in volume of the inclusion cavity, due to their relative compressibilities, would also be negligible.

(4) The fluid inclusions are primary or can be distinguished from secondary or subsequent inclusions.

Inclusions of type 1 are apparently primary. They probably occur on the $\{10\bar{1}1\}$ planes, and although very irregular in outline, do in some cases tend to have a negative crystal shape. Constancy of the degree of filling of the inclusions (all one-phase at room temperature) also indicates a primary origin. It is conceivable, though, that these inclusions are the result of later solutions, reflecting a lower temperature environment, which under pressure penetrated the calcite along these planes. Inasmuch as liquid cannot be forced out of the inclusions, unless through fractures, it seems improbable that it could be forced into the inclusions, under the very low pressure differentials that might have existed after crystallization. Inclusions of type 2, which occur in gently curving and intersecting planes in random distribution, apparently formed subsequently to the calcite, but under similar pressure-temperature conditions.

(5) The pressure at the time of formation was low or its magnitude can be estimated.

The available data indicate that the overburden at the time of formation was less than 1000 feet, equivalent to a maximum pressure of 85 bars if lithostatic, 30 bars if hydrostatic, or much less if the calcite was only under the vapor pressure of the mineralizing solutions. However, since the calcite formed in hollow geodes (Fig. 2) or in vugs, the crystals were not under lithostatic pressure during, or subsequent to, formation. Whatever the case, the pressure was negligible and no temperature correction is necessary.

Thus the fluid inclusions in calcite from geodes in the Harrodsburg

limestone indicate crystallization at temperatures between 25 and 40° C. Pressures during crystallization were correspondingly low, and definitely not exceeding a maximum of 30 bars.

Some evidence of environmental conditions during formation of the geodes is furnished by the presence of apparently primary inclusions of anhydrite in the massive quartz forming the geode shell and in the later quartz euhedra. According to MacDonald (1953) anhydrite is precipitated from natural sea water above a minimum temperature of about 34° C. If the anhydrite were deposited from a solution containing only CaSO_4 , this temperature would be 40° C. Pressure, at least up to 100 bars, has little effect on this temperature. Regardless of whether the quartz and anhydrite were precipitated from a sea of Mississippian age or from later ground water solutions (evidence favors the latter), the lower temperature limit for the formation of anhydrite agrees well with the range of temperature of formation of the calcite given above. No upper limit can be established, but unless unusual conditions prevailed, there was probably no significant change in the temperature conditions between the crystallization of the quartz and anhydrite and the subsequently deposited calcite, smythite, and pyrrhotite.

PYRRHOTITE

The pyrrhotite associated with smythite is the strongly ferromagnetic, monoclinic modification. The powder pattern of this material, shown in Table 1, agrees very well with that of the synthetic β_3 -phase, Fe_7S_8 , prepared by Grønvold and Haraldsen (1952). As was previously stated, pyrrhotite from Bloomington was determined to contain nickel by means of x -ray fluorescence analysis. Crystals of pyrrhotite are euhedral hexagonal plates and range in size from a diameter of 0.05 mm. to about 2 mm. or nearly double the size of the largest smythite crystals. It is difficult to distinguish between the associated pyrrhotite and smythite, but pyrrhotite appears to be more bronze and less black against a white background. It is brittle and plates in calcite are bent or broken and not curved as are those of smythite. The color in vertically reflected light is pinkish cream; anisotropism of prismatic sections is strong with yellow and blue-gray interference colors; weakly pleochroic from pale to brownish yellow.

The occurrence of this low-temperature pyrrhotite seems, in most respects, similar to other such reported occurrences of pyrrhotite from sedimentary rocks. Many of these have been summarized by Rosenthal (1956), but several others should be mentioned. Julien (1886) described "amorphous" black iron sulfide from the marshes of New Jersey and elsewhere, and Andrushev (1897) also described globules of ferrous sulfide

from muds of the Black Sea. Blatchley (1903) mentioned black flakes of iron sulfide in some of the strongly sulfurated springs and wells of Indiana. Pyrrhotite was specifically identified by Smyth (1911) as occurring in the upper part of the Clinton formation of Silurian age, near Lairds-ville and at Clinton, New York. Here it is associated with calcite and dolomite in quartz-lined cavities in calcareous hematitic sandstone. Dale (1953) has also described this occurrence and has done experimental work on the pyrrhotite. The powder pattern of pyrrhotite from Lairds-ville is identical with that of pyrrhotite from Bloomington shown in Table 1. Smythite was not found in a specimen (Princeton Collections no. 16/74) from this locality. Davies (1912) found pyrrhotite as an authigenic mineral in the Arctic Bed, a marsh deposit of late Pleistocene age, in the Lea Valley, Ponder's End, Middlesex, England. Hatch and Rastall (1923) noted pyrrhotite as occurring in shales. Milner (1929) mentioned several reported occurrences of pyrrhotite as an authigenic mineral in sediments and he (1940) identified the mineral in various British soils. Rubey (1930) described pyrrhotite from a pyritic and gypsiferous limestone, the Greenhorn formation of Late Cretaceous age, in the Black Hills region of Wyoming and Montana. Tamayo (1955) described authigenic low-temperature pyrrhotite, intimately associated with pyrite and marcasite, transecting calcareous foraminiferal shells and coarsely crystalline calcite in the lower Tortonien clay of Miocene age from many localities in the "gypsum-sulfur" regions of Sicily. Stanton (1955) reported pyrrhotite and chalcOPYrite in tuffaceous carbon-bearing shales, the uppermost members of the Triangle Creek Group which underlie the Rockley Volcanics of Late Ordovician (?) age, in the Rockley district, New South Wales. The pyrrhotite, according to Stanton, resulted from metamorphism of FeS_2 which was originally deposited by bacterial action during sedimentation.

Unfortunately x -ray powder data have not been given for these occurrences. It would be interesting to know whether the strongly ferromagnetic monoclinic or the weakly ferromagnetic hexagonal pyrrhotite is the more common in sedimentary rocks. The study of Kiskyras (1950) indicates that the strongly magnetic form predominates in low-temperature material, but since both monoclinic and hexagonal phases can be formed and are stable at room temperature (Allen *et al.*, 1912; Grønvold and Haraldsen, 1952), either might be expected to occur in this environment depending upon the concentration of sulfide ion present. Oftedahl (1955), by optical methods, detected low-temperature pyrrhotite in a black, bituminous, shale of Cambrian age at Oslo, Norway. However, he could not obtain an x -ray pattern of either hexagonal or monoclinic pyrrhotite from this material. A magnetic pyrrhotite, reported from

clays of Lower Jurassic age of the German-Holland border region by Hoffman (1948), has a composition close to $\text{Fe}_{11}\text{S}_{12}$ which suggests that it might be the hexagonal phase, but again, x-ray data are not available.

ORIGIN

Some clues as to the origin of smythite and pyrrhotite emerge from the preceding discussions. The sulfides are epigenetic, being deposited in the geodes after they were fractured; they crystallized simultaneously with the enclosing calcite (there is no evidence of replacement) which suggests that the depositing solution was neutral or weakly alkaline; they were formed in a trapped solution supplied with mineralizing ions by percolation and probably slow diffusion through pores and crevices in the surrounding rock and geode shell; the temperature during formation was between 25 and 40 ° C. and the pressure was low.

The source of iron seems most likely to have been FeS_2 , disseminated in the lower Harrodsburg limestone and Edwardsville formation, which was oxidized to produce iron sulfate as an end product. The sulfur may also have been supplied by the disseminated FeS_2 , for Mapstone (1954) found experimentally that both FeS and H_2S are formed as intermediate products in the weathering of pyrite by oxidation. Another possible source of sulfur is as H_2S transported by ground water and derived from buried organic matter, including petroleum, or from connate waters carrying the gas in solution. Blatchley (1903) mentioned several wells in the area containing dissolved H_2S . The total amount of iron and sulfur available to form smythite and pyrrhotite was small in any event, as they are present only in minute quantities.

Smythite and pyrrhotite seem to have preferentially nucleated directly on the growing calcite rather than to have grown in the solution in the geode and indiscriminately settled on calcite, dolomite, and quartz. Some crystals of both pyrrhotite and smythite can be found on, and in, other minerals, but the preponderance of the sulfides in the calcite and the tendency toward orientation supports this hypothesis.

ACKNOWLEDGMENTS

We thank Dr. Brian H. Mason and Dr. Gunnar Kullerud for helpful comments; Dr. Harry H. Hess and Princeton University for their loan of pyrrhotite from New York; Dr. George S. Switzer and the U. S. National Museum for their loan of valleriite from Sweden; and Dr. Fredrik Grønvold for his donation of samples of synthetic and natural pyrrhotites.

We are indebted to our colleagues at the U. S. Geological Survey; to George T. Faust for helpful advice; to Fred A. Hildebrand for compari-

sons of powder patterns of hexagonal and monoclinic phases of pyrrhotite; to Isadore Adler for the analyses by x-ray fluorescence spectrometry; and to Charles Milton for an examination of a polished section of smythite.

APPENDIX

EXPERIMENTAL ATTEMPTS TO SYNTHESIZE SMYTHITE

Attempts to synthesize smythite from various systems yielded no products which could be related to smythite, but it was felt that the experiments were of sufficient interest to warrant brief description. X-ray powder data for the solid phases obtained are given in Table 4.

TABLE 4. X-RAY POWDER DATA FOR SYNTHETIC PRODUCTS

FeK α radiation; 114.6 mm. dia. camera

Expt. 1		Expt. 2		Expt. 3	
<i>d</i> (obs.)	<i>I</i>	<i>d</i> (obs.)	<i>I</i>	<i>d</i> (obs.)	<i>I</i>
6.3	2	8.1	10	7.0	7
3.49	6	6.1	4	5.34	6
2.98	6	5.37	9	4.57	4
2.32	4	4.02	4	2.89	6
1.84	7	2.94	4	2.31	2
		2.76	6		

Note: all lines are broad.

Experiment 1. A black magnetic opaque material and pyrite were formed from a dilute solution of FeSO₄ saturated with H₂S and brought to a pH of 8.5 with NH₄OH. The precipitate was leached with water, dried, and allowed to stand 45 days. No change was observed in the powder pattern after this time, but when heated to 170° C. the material gave a pattern of hematite, marcasite, and pyrite. The original product was also prepared in a variety of ways such as treatment of siderite with Na₂S, H₂S, and dilute H₂SO₄.

Experiment 2. A black magnetic opaque precipitate resulting from the reaction of solutions of FeCl₃ and Na₂S at a pH of 11. The product was leached with water and was still moist when rolled into a powder spindle. Material allowed to dry in air completely oxidized to goethite in a few days.

Experiment 3. Some of the product of experiment 2 was gently warmed, almost to dryness, and compressed in a steel mortar. This gave a material

which was more strongly ferromagnetic and apparently more stable than that of experiment 2 as it only completely oxidized to goethite after about one month. This material is identical with the black stain formed on calcite by Lemberg's test.

REFERENCES

- ALLEN, E. T., CRENSHAW, J. L., JOHNSTON, JOHN, AND LARSEN, E. S. (1912), The mineral sulphides of iron, with crystallographic study: *Am. Jour. Sci.*, 4th ser., **33**, 169-236.
- ANDRUSSOV, N. (1897), La Mer Noire: 7^e Congrès Géol. Internat., *Guide des Excursions*, fasc. **29**, 13 p.
- ALSEN, NILS (1923), Vorläufige Mitteilung über eine Untersuchung der Kristallstrukturen von FeS und NiS: *Geol. Fören. Stockholm. Förh.*, **45**, 606-609.
- BAILEY, S. W. AND CAMERON, E. N. (1951), Temperatures of mineral formation in bottom-run lead-zinc deposits of the Upper Mississippi Valley, as indicated by liquid inclusions: *Econ. Geol.*, **46**, 626-651.
- BIRCH, FRANCIS (1942), Handbook of physical constants: (Francis Birch, ed.) *Geol. Soc. America Spec. Paper*, **36**, 325 p.
- BLATCHLEY, W. S. (1903), The mineral waters of Indiana: *Indiana Dept. Geol. and Nat. Res.*, 26th Ann. Rept., 1901, 18, 88-89.
- BUDDINGTON, A. F. (1938), Memorial to Charles Henry Smyth, Jr.: *Geol. Soc. America Proc.*, (1937), 195-202.
- CAMERON, E. N., ROWE, R. B., AND WEIS, P. L. (1953), Fluid inclusions in beryl and quartz from pegmatites of the Middletown District, Connecticut: *Am. Mineral.*, **38**, 218-262.
- DALE, N. C. (1953), Geology and mineral resources of Oriskany quadrangle (Rome quadrangle): *New York State Museum Bull.*, **345**, 78-79.
- DAVIES, G. M. (1912), The mineral composition of the Arctic Bed at Ponder's End: *Geol. Soc. London Quart. Jour.*, **68**, 247-248.
- DE JONG, W. F., AND WILLEMS, H. W. V. (1927), Die Verbindungen Fe_3S_4 , Co_3S_4 , Ni_3S_4 , und ihre Struktur: *Zeits. anorg. u. allg. Chemie*, **161**, 311-315.
- EAKLE, A. S. (1922), Massive troilite from Del Norte County, California: *Am. Mineral.*, **7**, 77-80.
- ERD, R. C. (1954), The Mineralogy of Indiana, Master's Thesis Indiana University, 170 p.
- AND EVANS, H. T., JR. (1956), The compound Fe_3S_4 (smythite) found in nature: *Jour. Am. Chem. Soc.*, **78**, 2017.
- FIX, G. F. (1939), Mineralization in the Harrodsburg limestone: *Indiana Acad. Sci. Proc.* (1938), **48**, 124-128.
- FONTANA, C. (1927), Sulla indentità di struttura cristallina dei composti Fe_3S_4 e FeS: *Atti Accad. Lincei*, 6th ser., **5**, 579-581.
- GRØNVOLD, FREDRIK AND HARALDSEN, HAAKON (1952), On the phase relations of synthetic and natural pyrrhotites (Fe_{1-x}S): *Acta Chemica Scandinavica*, **6**, 1452-1469.
- HÄGG, GUNNAR AND SUCKSDORFF, INGRID (1933), Die Kristallstruktur von Troilit und Magnetkies: *Zeits. physikal. Chemie*, **B22**, 444-452.
- HATCH, F. H. AND RASTALL, R. H. (1923), The petrology of the sedimentary rocks, 2d ed., 201, 217, George Allen and Unwin, Ltd., London.
- HOFFMAN, KARL (1948), Vorkommen von Einfach-Schwefeleisen (Magnetkies) in Sedimentgesteinen: *Erdöl u. Kohle*, **1**, 231-232.
- INGERSON, EARL (1947), Liquid inclusions in geologic thermometry: *Am. Mineral.*, **32**, 375-388.
- JULIEN, A. A. (1886), The microscopical structure of the iron pyrites: *New York Microscopical Soc., Jour.*, **2**, 85-96.

- JUZA, ROBERT, BILTZ, WILHELM, AND MEISEL, KARL (1932), Das Zustandsdiagramm Pyrit, Magnetkies, Troilit und Schwefeldampf, beurteilt nach Schwefeldampfdrucken, Röntgenbildern, Dichten und magnetischen Messungen: *Zeits. anorg. u. allg. Chemie*, **205**, 273-286.
- KISKYRAS, D. A. (1950), Untersuchungen der magnetischen Eigenschaften des Magnetkies bei verschiedenen Temperaturen in besondern Hinblick auf seine Entstehung: *Neues Jahrb. Min. Geol., Abh.*, **80**, A, 297-342.
- LEPP, HENRY (1954), An experimental study of interconversions among iron carbonates, oxides, and sulfides: thesis at University of Minnesota, 108 p. Abstract in *Dissertation Abstracts*, **14**, 983.
- LIPIN, S. V. (1946), On the nature of pyrrhotite and troilite: *Soc. russe mineralogie Mem.*, **75**, 273-284.
- LUNDQVIST, DICK (1947), X-ray studies on sulphides of nickel and iron obtained by precipitation from water solutions: *Arkiv for Kemi, Mineralogi och Geologi*, **24A**, no. 23, 7 p.
- MACDONALD, G. J. F. (1953), Anhydrite-gypsum equilibrium relations: *Am. Jour. Sci.*, **251**, 884-898.
- MAPSTONE, G. E. (1954), The weathering of pyrite: *Chemistry and Industry*, 577-578.
- MERWIN, H. E. (1914), The simultaneous crystallization of calcite and certain sulphides of iron, copper and zinc. A crystallographic study: *Am. Jour. Sci.*, 4th ser., **38**, 355-359.
- MEUNIER, STANISLAS (1869), Étude minéralogique du fer météorique de Deesa: *Cosmos*, **5**, 581.
- MICHEL, ANDRE (1937), Propriétés magnétiques de quelques solutions solides, Chapter III. Le sulfuré ferreux et ses solutions solides: *Annales de Chimie*, 11th ser., **8**, 379-416.
- (1955), Étude de la réaction de l'hydrogène sulfuré sur les oxydes de fer, pt. I, Étude de la réaction de fixation et du produit de réaction: *Soc. Chimique de France, Bull.*, fasc. **10**, 1187-1188.
- AND MRS. CHOAIN (1956), Étude de la réaction de l'hydrogène sulfuré sur les oxydes de fer, pt. III. Réactivité des oxydes de fer anhydres et hydratés. Le phénomène de revivification: *Soc. Chimique de France, Bull.*, fasc. **3**, 453-455.
- MILLER, J. P. (1952), A portion of the system calcium carbonate-carbon dioxide-water with geological implications: *Am. Jour. Sci.*, **250**, 161-203.
- MILNER, H. B. (1929), Sedimentary petrography, 2d ed., 225, Thomas Murby and Co., London.
- (1940), Sedimentary petrography, 3d ed., 528, Thomas Murby and Co., London.
- OKAZAKI, ATSUSHI AND HIRAKAWA, KINSHIRO (1955). The x-ray study of FeSe₂, II: *Busseiron Kenkyu* No. **90**, 59-60.
- OFTEDAHL, CHR. (1955), On the sulphides of the alum shale in Oslo: *Norsk Geol. Tidsskrift*, **35**, 117-120.
- PEHRMANN, GUNNAR (1954), Über den Magnetismus einiger Magnetkiese: *Acta Acad. Aboensis, Math. et Phys.*, **19**, 3-8.
- RICHTER, D. H. AND INGERSON, EARL (1954), Some considerations regarding liquid inclusions as geologic thermometers: *Econ. Geol.*, **49**, 786-789.
- RODGERS, JOHN (1940), Distinction between calcite and dolomite on polished surfaces: *Am. Jour. Sci.*, **238**, 788-798.
- ROSENTHAL, GERNOT (1956), Versuche zur Darstellung von Markasit, Pyrit, und Magnetkies aus wässrigen Lösungen bei Zimmertemperatur: *Heidelberger Beitr. z. Mineralogie u. Petrographie*, **5**, 146-164.
- RUBEY, W. W. (1930), Lithologic studies of fine-grained Upper Cretaceous sedimentary rocks of the Black Hills regions: *U. S. Geol. Survey Prof. Paper* **165-A**, 6-7.

- SIDOT, TH. (1868), Sur la préparation des sulfures de fer et de manganèse: *Acad. Sci. Paris Comptes Rendus*, **66**, 1257-1258.
- SKINNER, B. J. (1953), Some considerations regarding liquid inclusions as geologic thermometers: *Econ. Geol.*, **48**, 541-550.
- SMITH, F. G. (1953), Historical development of inclusion thermometry, Univ. of Toronto Press, Toronto.
- SMYTH, C. H., JR. (1911), A new locality of pyrrhotite crystals and their pseudomorphs: *Am. Jour. Sci.*, 4th ser., **32**, 156-160.
- SORBY, H. C. (1858), On the microscopical structure of crystals, indicating the origin of minerals and rocks: *Geol. Soc. London Quart. Jour.*, **14**, 453-500.
- STANTON, R. L. (1955), The occurrence and paragenesis of pyrrhotite and chalcopyrite in sediments near Rockley, New South Wales: *Royal Soc. New South Wales Jour. and Proc.*, **89**, 73-77.
- STELZNER, A. W. (1896), Beiträge zur Entstehung der Freiburger Bleierz und der erzgebirgischen Zinnerz-Gänge: *Zeits. prakt. Geol.*, **4**, 400.
- STEVENS, R. E. (1933), The alteration of pyrite to pyrrhotite by alkali sulphide solutions: *Econ. Geol.*, **28**, 1-19.
- STROMEYER, FRIEDRICH (1814), Analyse zweier Magnetkiese, und Untersuchungen über den künstlichen Magnetkies: *Annalen der Physik*, **48**, 183-192.
- TAMAYO, ELEONORA (1955), Sur la présence de pyrrhotite de néoformation dans des argiles sédimentaires de Sicile: *Soc. Géol. France, Bull.*, 6th ser., **5**, 375-379.
- WASER, JURG (1951), The Lorentz and polarization correction for the Buerger precession method: *Rev. Sci. Inst.*, **22**, 567-568.
- WEIL, RENE (1955), Reproduction expérimentale des sulfides métalliques des sédiments biogènes: *Congrès Soc. Savantes Paris, Comptes Rendu, Sciences*, 80th, (1955), 117-125.

Manuscript received Sept. 24, 1956.

DETERMINATION OF THE COMPOSITION OF PLAGIOCLASE FELDSPARS BY MEANS OF INFRARED SPECTROSCOPY

C. SHELDON THOMPSON* AND MILTON E. WADSWORTH,† *University of Utah, Salt Lake City, Utah.*

ABSTRACT

A systematic variation in the infrared spectra of plagioclase feldspars throughout the albite-anorthite series indicates a definite correlation between the band positions, number of bands, and composition. A structural shift is indicated in the region An_{31} - An_{23} . Data are presented whereby composition may be determined by the wave length of the symmetry vibrational mode in the 15.4 to 16.2 micron region.

INTRODUCTION

The application of infrared spectroscopy to the study of inorganic systems has been very limited. The infrared spectra of a number of clay minerals have been studied in some degree (Adler, *et al.*, 1950; Keller and Pickett, 1950) and the applicability of the infrared method to other mineral systems has been demonstrated (Hunt, *et al.*, 1950; Keller, *et al.*, 1952; Hunt and Turner, 1953).

The possibility for the study of the plagioclase series was made apparent by the spectra published by Hunt, *et al.* (1950) of albite, oligoclase and anorthite which showed a marked difference in the number and positions of absorption bands for each of the above mentioned samples. Here it is shown that the composition of the plagioclase feldspars can be determined by the use of infrared spectroscopy and it is suggested that this method may prove valuable in the study of other isomorphous series.

PROCEDURE

The samples used were obtained from Dr. J. R. Smith (Geophysical Laboratory), Wards Natural Science Establishment and the Mineralogy Department, University of Utah (see Table 1). Identification of the samples, with the exception of four analyzed samples from J. R. Smith, was made by means of the four axis universal stage using the Berek method (1924) and checked by Turner's method (1947). The compositional error is believed to be within 2-3%. The infrared spectra were obtained using a Perkin-Elmer Model 21 double beam recording infrared spectrophotometer. A NaCl prism was used for the spectral region 2 to 15 microns and a KBr prism for the range 15 to 25 microns.

Each sample was prepared for infrared examination in a manner sim-

* Department of Geology, Westminster College, Salt Lake City, Utah.

† Associate Professor, Department of Metallurgy, University of Utah.

TABLE 1. COMPOSITION AND SOURCE OF PLAGIOCLASE SAMPLES

Number	% Anorthite	Host Rock	Source†	Location
13·4·30	5	Granite	U.U.	Unknown
13·4·7	15	Pegmatite	U.U.	Unknown
Wards #11	23	Pegmatite	W.N.S.E.	Bamle, Norway
Wards #5	26	Pegmatite	W.N.S.E.	Tvedestrand, Norway
13·3·5	28	Pegmatite	U.U.	Ontario, Canada
Wards #6	33	Quartz diorite	W.N.S.E.	Transvaal
Wards #2	35	Lava	W.N.S.E.	Japan
Wards #7	43	Anorthosite	W.N.S.E.	Labrador
Wards #12	50	Anorthosite	W.N.S.E.	New York
Wards #8	52	Anorthosite	W.N.S.E.	Lake St. John, Quebec
BV·63*	63	Gabbro	J.R.S.	Bushveld complex, S. Africa
13·1·19	67	Lava	U.U.	Clear Lake, Utah
EB·38*	85	Norite	J.R.S.	Stillwater complex, Montana
2·2·4	85	Anorthosite	U.U.	Stillwater complex, Montana
Wards #3	89	Hornblende Norite	W.N.S.E.	Grass Valley, California
EB·18*	91	Norite	J.R.S.	Stillwater complex, Montana
Wards #4	94	Lava	W.N.S.E.	Miakejima, Japan
HGIF AN 53*	94	Veinlike mass in schist	J.R.S.	Greenland

* Analyzed samples as follows:

Analysts: Samples BV·63, HGIF·AN·53 by Eileen Oslund, Rock Analysis Laboratory, Minnesota (Unpublished to date).

Samples EB·38, EB·18 by A. H. Phillips, Princeton University. (Published by Kracek and Neuvonen, *Am. Jour. Sci.*, Bowen Volume).

Samples BV·63, EB·38, EB·18 were collected by H. H. Hess, Princeton University.

† U.U., Univ. of Utah collection; W.N.S.E., Ward's Nat. Sci. Estab.; J.R.S., J. R. Smith, Geophysical Lab., Wash., D. C.

ilar to the procedure presented by French, et al., (1954) using the pressed pellet technique. A one gram KI plate, 22 mm. in diameter, containing 2 mg. of sample, was found to be most satisfactory in exploring the whole spectral range of 2 to 25 microns. For a detailed study of certain regions of the spectra, 4 mg. of sample were used per plate. The KI used was recrystallized and a one gram plate of pure KI was placed in the reference beam to compensate for any impurities present.

RESULTS AND DISCUSSION

In the preliminary examination, three groups of definitive absorption bands were found at 8.5 to 11 microns, 12 to 15 microns and 15 to 19

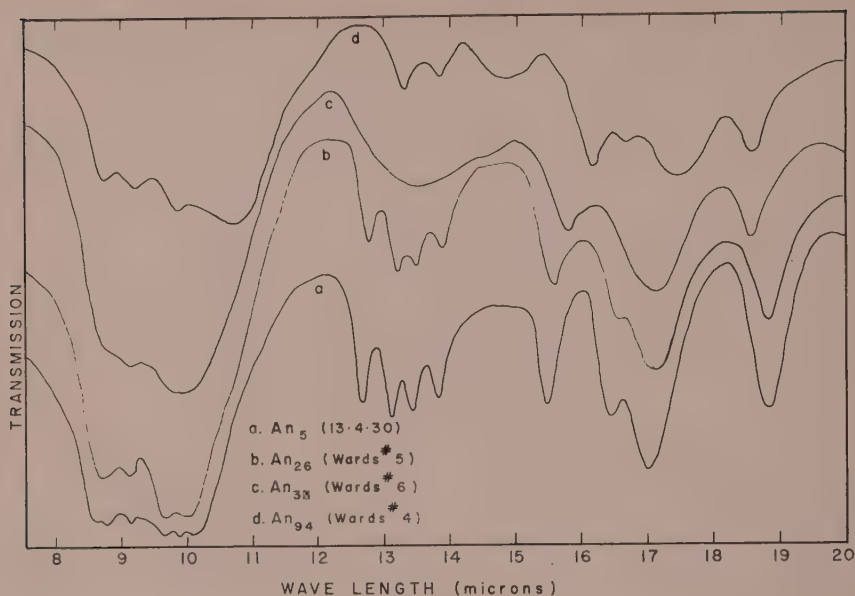


FIG. 1. Infrared spectra of plagioclase feldspars of various composition in the wave length region 8-20 microns.

microns, Fig. 1. These groups were examined more closely by expanding the spectral scale of the instrument. In each of the three groups, changes in number or position of the absorption bands were noted, corresponding to the changes in the composition of the sample. Two gross structural changes in the plagioclase series appear in the composition ranges An_{28} – An_{33} and An_{67} – An_{85} . This is evident from the curves of Fig. 1 and the tabulated data of Table 2.

One band (15.4–16.2 microns) was observed to shift consistently toward the longer wave lengths as the sample composition increased in anorthite content. Figure 2 is a plot of the measured wave length of this band versus composition. The extrapolated intersection of the two regions of this curve more closely fixes the composition of the structural shift indicated between An_{28} and An_{33} according to the gross variations of the spectra of Fig. 1. It appears that the lower limit of this shift is approximately An_{31} . Such a break may be interpreted as a structural shift resulting in an abrupt variation of some of the lattice frequencies. The data used to plot Fig. 2 was recalculated and presented in Fig. 3.

The solid curve of Fig. 3 represents the increment ($\Delta\lambda$) in wavelength between the 15.4 to 16.2 micron feldspar band and the 14.99μ CO_2 band versus the silicon to aluminum molar ratio. This shift is useful because

TABLE 2. POSITIONS OF ABSORPTION BANDS

Number	% Anorthite	8.5 to 11 Micron Region						12.5 to 15 Micron Region				15 to 19 Micron Region			
		8.78M	9.16S	9.65S	9.85S	10.06S	12.73S	13.16S	13.46S	13.86S	15.44S	16.46S	16.98S	18.82S	18.82S
13 · 4 · 30	5	8.77M	9.12S	9.68S	9.95S	10.06S	12.75S	13.20S	13.50S	13.80S	15.50S	16.48M	17.06S	18.74S	18.74S
13 · 4 · 7	15	8.77S	9.13S	9.67S	9.91M		12.75S	13.20S	13.50S	13.85S	15.52S	16.52W	17.02S	18.77S	18.77S
Wards #11	23	8.75M	9.11S	9.67S	9.91S		12.72S	13.15S	13.48S	13.80S	15.54S	16.44W	17.06S	18.74S	18.74S
Wards #5	26	8.81M	9.12S	9.67S	9.91S		12.75S	13.20S	13.50S	13.80S	15.54S	Weak	17.06S	18.74S	18.74S
13 · 3 · 5	28		9.13S	9.88S					13.50S		15.78S		17.06S	18.58S	18.58S
Wards #6	33		9.18S	9.85S			12.52W	12.84S	13.40S		15.89S		17.18S	18.46S	18.46S
Wards #2	35		9.09S	9.99S				12.90W	13.40S		15.98S		17.28S	18.50S	18.50S
Wards #7	43		9.19S	10.00S					13.40S	14.80W	15.98S		17.26S	18.58S	18.58S
Wards #12	50	8.75W	9.07S	10.03S				12.85W	13.36M		16.00S		17.28S	18.50S	18.50S
Wards #8	52		9.17S	10.08S				12.90W	13.50S		16.06S		17.26S	18.58S	18.58S
BV · 63*	63		9.14S	10.03S					13.28S		16.08S		17.24S	18.52S	18.52S
13 · 1 · 19	67	8.75W	9.18S	9.88S					13.25S	13.74S	16.12S	16.57W	17.40S	18.60S	18.60S
EB · 38*	85	8.76S	9.17S	9.90S	10.12S	10.66S			13.25S	13.70S	16.12S	Weak	17.50S	18.56S	18.56S
2 · 2 · 4	85	8.73S	9.21S	9.83S	10.09S	10.72S			13.25S	13.75S	16.12S	16.62M	17.52S	18.56S	18.56S
Wards #3	89	8.76S	9.17S	9.82S	10.12M	10.73S			13.25S	13.72S	16.14S		17.40S	18.60S	18.60S
EB · 18*	91	8.79S	9.24S	9.88S	10.14S	10.70S			13.30S	13.80S	16.14S	16.61M	17.34S	18.54S	18.54S
Wards #4	94	8.76S	9.25S	9.85S	10.08M	10.77S			13.25S	13.76S	16.16S	16.60M	17.40S	18.62S	18.62S
HGIF · AN · 53*	94					10.75S									

S—Strong, M—Medium, W—Weak.

* Analyzed samples (see Table 1).

of the close proximity of the CO_2 band which acts as a calibration for the measured shift and tends to normalize results without extreme care in terms of absolute wavelength. The dotted curve of Fig. 3 represents the relationship between the Si/Al molar ratio and the weight per cent of anorthite. This plot also suggests the possibility that the structural change in the region, An_{28} – An_{33} gives rise to a skeletal frequency due to

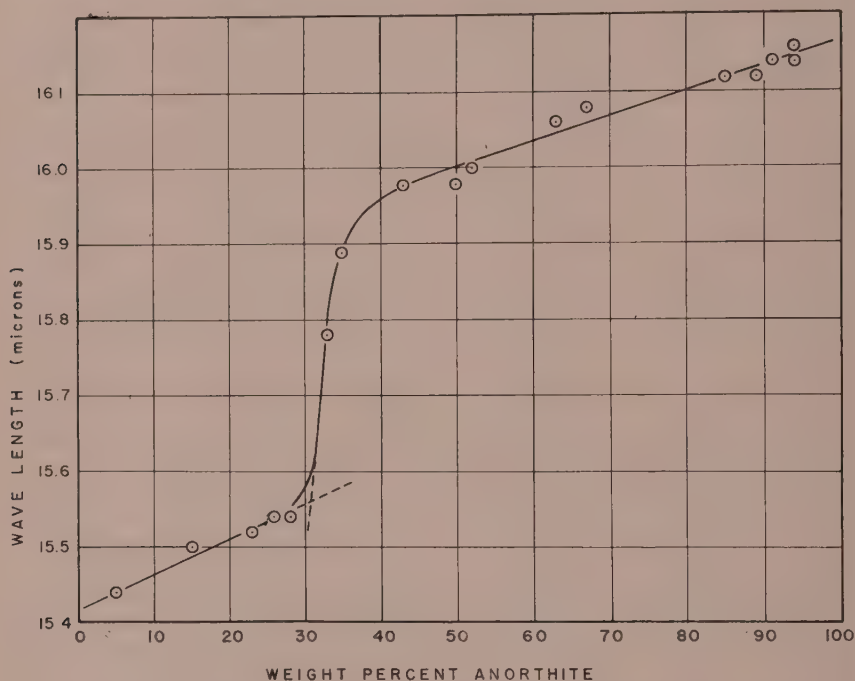


FIG. 2. Correlation of the wave length of the infrared band in the 15.4–16.2 micron region with per cent anorthite for plagioclase feldspars of various composition.

an ordered structure at a Si/Al ratio of 2:1, halfway between the albite ratio of 3:1 and the anorthite ratio of 1:1. The existence of structural changes was demonstrated by Chao and Taylor (1940) within the ranges of An_{22} – An_{57} and An_{67} – An_{80} ; also Cole, Sorum and Taylor (1951) stated that plagioclases up to the composition An_{30} are isomorphous with the albite structure but that the exact limit of isomorphism is obscure. They also state that the composition An_{72} is the lower limit for plagioclases which are isomorphous with the anorthite structure. There is no evidence of a structural shift in the region An_{67} – An_{85} in the infrared data presented in Fig. 2. It is conceivable, however, that a structural shift may occur

without affecting the frequency mode corresponding to the absorption band in the 15.4–16.2 micron region.

Table 2 gives the positions of all the absorption bands which occur in the three regions under consideration. In light of the data available at present, infrared spectra do not appear to distinguish between high and low temperature plagioclases. The data for both high and low tempera-

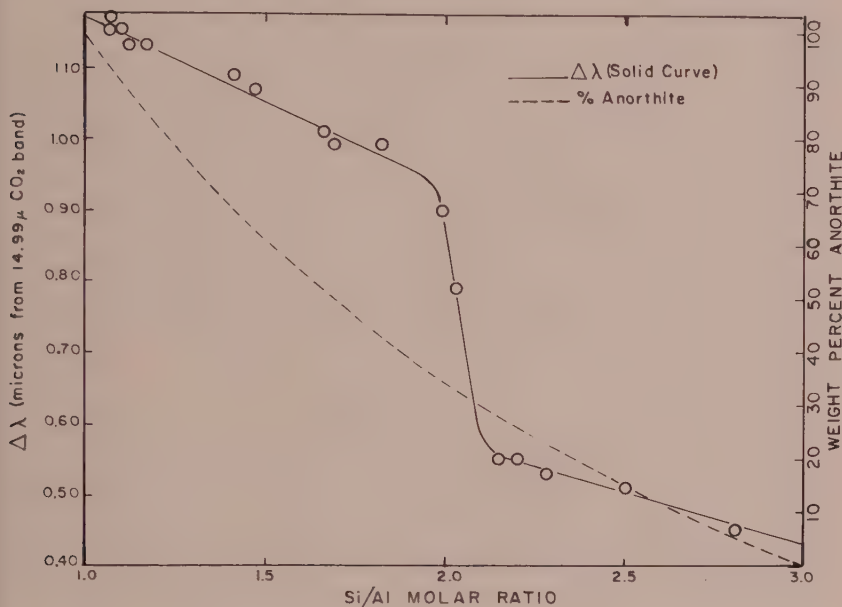


FIG. 3. Correlation of the position of the infrared band in the 15.4–16.2 region (relative to the CO₂ band at 14.99 μ) with the Si/Al molar ratio and with the weight per cent anorthite.

ture forms (Table 1—inferred by host rock) are well correlated as is evident by the curve of Fig. 2. Therefore, it is suggested that this method may be more useful than other methods which are hampered by this problem.

Some attempt has been made to correlate the vibrational frequencies of the plagioclase feldspars with those of alpha quartz as presented by B. D. Saksena (1940). Alpha quartz exhibits three absorption bands (8.63 microns, 8.7 microns and 9.40 microns) which seem to correspond approximately with the plagioclase bands in the 8.5–11 micron region. Saksena has assigned the following symmetry modes to the above mentioned bands: 8.63 microns, deformational oscillation of oxygen atoms in the basal planes; 8.71 microns, valence oscillation of oxygen atoms;

9.40 microns, oscillation of oxygen and silicon atoms along the optic axis. There are also four alpha quartz absorption bands in the 12–15 micron region with symmetry modes assigned as follows: 12.04 microns and 12.58 microns, oscillation of oxygen atoms along the optic axis; 12.86 microns, radial motion of oxygen atoms; 14.55 microns, translational oscillation of oxygen atoms against each other in the basal planes.

There appears, therefore, to be a general similarity between the infrared spectra of quartz and the plagioclase feldspars, particularly in the 8–15 micron region. In the 15–19 micron region several additional bands appear which are not present in the quartz spectrum. The 15.4–16.2 micron band which has been shown to vary systematically through the entire plagioclase series is among the latter group. Consequently, it is not possible to describe the character of this particular symmetry mode by comparison with the quartz spectrum. The closest quartz band is the 14.55 micron translational oscillation band. The increased complexity of the plagioclase spectra compared to quartz is expected because of the lower order of symmetry of the triclinic system and because of the substitution of aluminum for silicon atoms in the tetrahedral positions.

CONCLUSIONS

It appears from the results of this study that the positions of the symmetry mode in the plagioclase feldspars giving rise to an absorption band in the 15.4–16.2 micron region of the infrared spectrum is a direct indication of composition. Also the position of this particular band does not appear to be influenced by the high or low temperature history of the sample. A definite structural shift is indicated at a composition of approximately An_{31} – An_{33} , and a gross examination of several spectra indicates a second structural shift in the An_{67} – An_{85} region.

ACKNOWLEDGMENTS

The authors wish to extend appreciation to the University of Utah Engineering Experiment Station for supplying funds necessary to carry out this study. Thanks are also extended to: J. R. Smith (Geophysical Laboratory, Washington, D.C.) and H. H. Hess (Princeton University) for supplying analyzed feldspar samples; to the Department of Mineralogy, University of Utah for supplying all additional samples; and to the Kennecott Copper Corporation who made possible the purchase of the Perkin-Elmer Model 21 infrared spectrophotometer used in this study through a grant to the College of Mines and Mineral Industries.

Special appreciation is extended to Bronson F. Stringham, Head, Department of Mineralogy, University of Utah for his interest, suggestions and encouragement in this study.

ADDENDUM

Since the writing of this paper, an article has come to our attention by George W. DeVore (*Zeits. Krist.*, **107**, 247–264, 1956) which concludes, on the basis of bond energy changes, that the mineral An·33.3 represents a high degree of ordering in the Si-Al positions, and that “An·33.3 and anorthite are interpreted as unique compounds in the plagioclase series.”

REFERENCES

- ADLER, H. H., KERR, P. F., BRAY, E. E., STEPHENS, N. P., HUNT, J. M., KELLER, W. D., AND PICKETT, E. E. (1950), Infrared spectra of reference clay minerals: *Am. Petroleum Inst., Project 49*, Prelim. Report No. 8.
- BEREK, M. (1924), *MIKROSKOPISCHE MINERALBESTIMMUNG MIT HILFE DER UNIVERSAL-DRECHTISCHMETHODEN*, Verlag von Gebrüder Borntraeger, Berlin.
- CHAO, S. H., AND TAYLOR, W. H. (1940), Isomorphous replacement and superlattice structures in the plagioclase feldspars: *Roy. Soc. of London Proc., Series A*, **176**, 76–87.
- COLE, W. F., SORUM, H., AND TAYLOR, W. H. (1951), The structures of the plagioclase feldspars I: *Acta Cryst.*, **4**, 20–29.
- FRENCH, R. O., WADSWORTH, M. E., COOK, M. A., CUTLER, I. B. (1954), The quantitative application of infrared spectroscopy to studies in surface chemistry: *J. Phys. Chem.*, **58**, 805.
- HUNT, J. M., WISHERD, M. P., AND BONHAM, L. C. (1950), Infrared absorption spectra of minerals and other inorganic compounds: *Anal. Chem.*, **22**, 1478–1497.
- HUNT, J. M., AND TURNER, D. S. (1953), Determination of mineral constituents of rocks by infrared spectroscopy: *Anal. Chem.* **25**, 1169–1174.
- KELLER, W. D., AND PICKETT, E. E. (1950), The absorption of infrared radiation by clay minerals: *Am. J. Sci.*, **248**, 264.
- KELLER, W. D., SPOTTS, J. H., AND BIGGS, D. L. (1952), Infrared spectra of some rock forming minerals: *Am. J. Sci.*, **250**, 453–471.
- SAKSENA, B. D. (1940), Analysis of Raman and infrared spectra of alpha quartz: *Indian Academy of Sci. Proc.*, **12**, 93–139.
- TURNER, F. J. (1947), Determination of plagioclase with four-axis universal stage: *Am. Mineral.*, **32**, No. 7–8.

Manuscript received Aug. 13, 1956.

KOBEITE FROM PARINGA RIVER, SOUTH WESTLAND, NEW ZEALAND

C. OSBORNE HUTTON, *Stanford University, California.*

ABSTRACT

A tantalum-niobium-titanium-bearing mineral has been found as slender prismatic crystals in a cobble of graphic granite in gravels of the Paringa River, South Westland, New Zealand. The mineral is dark brown in color and metamict with the characteristic resinous luster and strikingly conchoidal fracture of a mineral in that physical state. The refractive index is 2.205 but after being heated to 1200° C. in vacuo a value of 2.35 was recorded; specific gravity is close to 5. X-ray diffraction patterns secured from unheated and carefully heated fragments are either identical to or exhibit insignificant differences from powder photographs obtained with similarly treated kobeite from the type locality of Shiraishi, Kyoto Prefecture, Japan. On the basis of these details but in the absence of quantitative analytical data, the South Westland mineral is considered to be identical, or very closely related to, kobeite. The source of the pebble is uncertain but it has probably been derived from granitic stocks or pegmatites that are known to outcrop in this general area.

OCCURRENCE

The kobeite-bearing cobble, 75 mm. in diameter, was collected while panning sands and gravels in the Paringa River, South Westland, New Zealand, at a point approximately $\frac{3}{4}$ of a mile upstream from the bridge on the Weheka-Paringa highway. The mineral occurs as very dark brown prismatic crystals that extend intermittently over distances of 30–45 mm. with a sheaf-like or radiating arrangement (Figs. 1 and 2) that rather strikingly resembles Figs. 1*a* and 1*b* in Takubo, Ukai, and Minato's (1950) paper on kobeite. The matrix consists of a coarse aggregate of oligoclase and microcline with a rude micrographic relationship; very rare quartz, epidote, muscovite, and chlorite complete the mineral assemblage.

MINERALOGY

In transmitted light the mineral is deep coffee brown, sometimes semi-opaque, and by reflected light a bright resinous luster and strongly conchoidal fracture surfaces are evident. Crystals are either long prismatic when they are clear and transparent, or stumpy and irregular in form with a tendency to exhibit irregularly distributed areas of much darker brown color; these zones may be shown to be much more radioactive than the more translucent portions of the crystals (Fig. 3). This situation is not dissimilar from that found for manganoan allanite from Yosemite National Park (Hutton, 1951, p. 242), and several other localities (Marble, 1948, pp. 80–85). Crystals are coarsely striated parallel to their lengths and pronounced cross-fracture is evident in thin section and crushed material.

The mineral is metamict and under strong illumination an almost imperceptible birefringence may be detected. The refractive index, measured several times in sulfur-selenium glasses, has an average of 2.205 ± 0.005 . After the mineral has been heated at 1200°C . for $2\frac{1}{2}$ hours in vacuo the refractive index increases to 2.35 ± 0.01 , and at the same time a strong aggregate birefringence becomes evident. The mineral exhibits

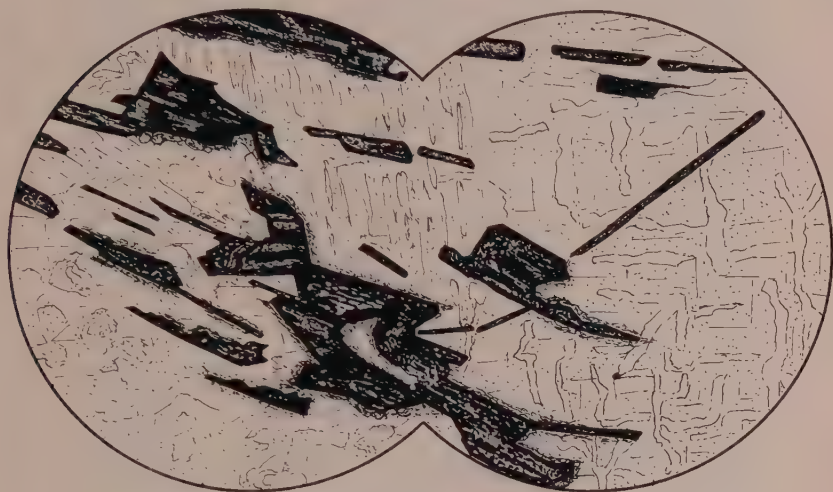


FIG. 1. Regularly arranged prismatic crystals of kobeite in a matrix of micrographically related microcline and oligoclase from Paringa River, South Westland, New Zealand. Magnification $\times 65$.

no superficial alteration¹ as does Japanese kobeite, but boundary zones between crystals and enclosing feldspar are very often distinctly stained brown, probably as a result of oxidation of iron freed from the mineral during metamictization. Owing to the limited amount of material available, specific gravity determinations have not been successfully carried out beyond noting that particles appeared to sink after twelve hours suspension in a melt of thallous formate and thallous malonate; accordingly one may only report that the specific gravity of the Paringa mineral is probably slightly in excess of 5.

¹ An x-ray powder film of the yellow alteration material that surrounds crystals of Japanese kobeite indicates that anatase is the chief constituent with line diffuseness that suggests extremely fine particle size; slightly larger d -spacings than those recorded for pure anatase (Swanson and Tatge, 1953, p. 46) may be attributed to ionic substitution of Ti^{4+} ions by the larger Ta^{5+} and Nb^{5+} ions. A few additional rather strong lines present are not attributable to associated minerals.

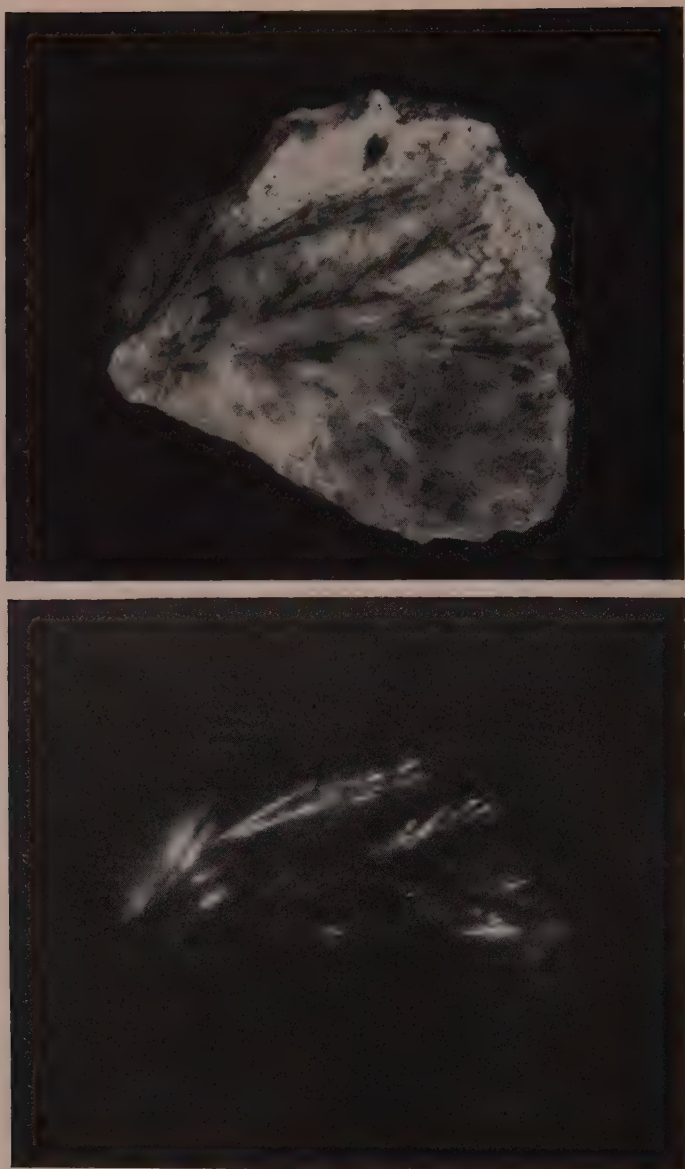


FIG. 2 (top). Polished surface of micrographic granite that exhibits radiating aggregates of prismatic crystals of kobeite from Paringa River, South Westland, New Zealand. Dimension from top to bottom of the rock surface is 70 mm.

FIG. 3 (bottom). Autoradiograph of Paringa River kobeite as exposed on polished surface illustrated in Fig. 2. Exposure period was 72 hours.

CHEMICAL COMPOSITION

It is unfortunate that scarcity of material permitted only qualitative chemical tests to be made. Rare earths, tantalum, niobium, and titanium were found to be present in considerable amounts, and the color of the flocculent tannin-complex precipitate devoid of titanium obtained by leaching potassium bisulphate fusions with 1 per cent tannin solution in 5% H_2SO_4 was reddish-orange in color, a condition that points to dominance of niobium over tantalum. The presence of iron, oxidation state unknown, aluminum, uranium, thorium, and water was verified.

The Paringa River mineral is apparently insoluble in hot concentrated HCl after long treatment, but some reaction is evident with hot concentrated H_2SO_4 . It is readily soluble in fused potassium bisulphate. With a concentrated oxalic acid solution at about 100°C . no noticeable effect was evident with either the Paringa River mineral or with Japanese kobeite. On the other hand, 5 minutes treatment with 1:1 HF in the cold caused slight iridescent films to develop on the bright conchoidal fracture surfaces of the Paringa River mineral, and thin greyish-white opalescent crusts appeared rather patchily developed on Japanese kobeite. With cold concentrated HF the effect was only very slightly more evident in each instance. In their reactivity towards oxalic acid and HF these two minerals differ from what is usually found for polycrase-euxenite, eschynite-priorite, fergusonite, or samarskite, since considerable reaction occurs with the latter minerals.

X-RAY STUDY

Powder cameras of 114.59 mm. diameter and nickel-filtered copper radiation were employed exclusively in this work; and in addition it should be understood that a single fragment, 0.1–0.2 mm. in diameter, mounted on a glass fiber was used in each instance as the diffraction material rather than powdered specimens.

Pure fragments of the Paringa River mineral and kobeite from Japan have been subjected to heat-treatment as follows: (1) Samples, in platinum microcrucibles, were placed in an already-heated furnace at 620°C . and at 1200°C .; accordingly these samples were heated in contact with air. (2) Samples were sealed in Vycor or silica capillaries in vacuo and then heated at the same temperatures as before, and in addition at 900°C . and 1000°C . All samples were x -rayed after having cooled to room temperature.

Paringa River material untreated in any way, gives weak, usually diffuse powder lines (Table 1, column A) after an exposure of 24 hours; this diffraction pattern, which was found to be quite reproducible, appears indicative of remnants of a primitive cubic structure, cell edge

about 14.3 Å, that may have existed before metamictization, and at the same time the utterly disoriented nature of the mineral is clear. With material heated in air and in vacuo at 620° C. new patterns are obtained that are closely similar to one another, and except for two or three exceedingly faint lines that are not permitted by the space-group, the spacings may be compared to those of a cubic face-centered uraninite-type of pattern with cell edges of 5.029 Å and 5.021 Å respectively

TABLE 1. X-RAY DIFFRACTION PATTERNS YIELDED BY UNHEATED FRAGMENTS OF THE PARINGA RIVER MINERAL (A) AND KOBETTE, JAPAN (B)

Radiation $\text{CuK}\alpha=1.5418$ Å. Intensities determined visually

A		B	
<i>d</i> , meas. Å	<i>I</i>	<i>d</i> , meas. Å	<i>I</i>
4.50	<1	4.50	<1
4.16	3	4.16	3
3.75	1	3.74	1
3.50	<1	3.50	<1
3.32	<1	3.35	<1
3.20	1	3.13	1
—	—	2.55	<1
—	—	2.18	<1
—	—	2.10	<1
—	—	1.74	<1

(Tables 2 and 3). Careful comparison of these films with powder patterns of reverted microlite reveals an absence of several fairly strong lines of the latter in the former; consequently the patterns of the Paríngá River mineral are considered to be more comparable to a uraninite-type rather than to that of microlite-pyrochlore with cell edges of 10.058 Å and 10.042 Å in which the strongest lines only are developed. It is interesting to note that heating in contact with air has permitted a slightly larger cell to develop; this increase in size is probably due to oxygen intake during the heating process.

After being heated in air or in vacuo at 1200° C. fragments of the Paríngá River material give distinctive x-ray diffraction patterns that are closely similar to one another (Table 4); particle size has increased because most of the lines are now quite sharp. In each case the three strongest lines of the uraninite-type pattern, viz. (111), (200), and (311), persist in the new patterns, although not at the same relative intensities, whereas the strong reflection (220) appears to coincide with or be very

close to a line that is usually almost imperceptible in the new patterns. Attempts to index these films systematically were unsuccessful and this fact leads one to the conclusion that two or more phases may be present, although the degree of simplicity in the patterns may be an argument

TABLE 2. X-RAY DIFFRACTION POWDER PATTERNS OF PARINGA RIVER MATERIAL AND KOBITE, JAPAN

All samples heated for one hour at 620° C. Radiation $\text{CuK}\alpha = 1.5418 \text{ \AA}$

A		B		C		D	
<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>
4.15	1	4.15	1	4.15	<1	4.14	1
3.76	<1	3.74	1	—	—	3.76	<1
2.89	10	2.89	10	2.90	10	2.89	10
2.505	4	2.508	5	2.514	5	2.506	4
1.777	8	1.772	8	1.778	8	1.776	8
1.516	7	1.513	7	1.517	7	1.514	7
1.453	1	1.447	1	1.451	1	1.452	1
1.255	1	1.254	1	1.256	1	1.257	1
1.154	2#	1.153	3#	1.156	3#	1.154	3#
1.125	2#	1.124	3#	1.126	3#	1.126	3#
1.028	1#	1.026	2#	1.028	2#	1.027	2#
.969	1#	.967	2#	.968	2#	.969	2#
—	—	.888	<1	.890	<1	—	—
.851	<1#	.850	2#	.850	3#	.851	2#
.838	2#	.839	3#	.838	1#	.838	2#

Diffuse lines.

A. Kobeite, Japan, heated in vacuo.

B. Paringa River material, heated in vacuo.

C. Paringa River material, heated in air.

D. Kobeite, Japan, heated in air.

against this suggestion. Certainly there was no indication of any lines due to rutile, brookite, or pseudobrookite.

The *x*-ray films obtained with the Paringa River mineral after being heated to 1200° C. have been compared with those obtained from a large number of multiple oxides of tantalum, niobium, titanium, and rare earths, but this provided no clue as to the true identity of the mineral in question, although it may be pointed out that a number of minerals belonging to this general group do give *x*-ray powder patterns of the uraninite-type after being heated to 620° C. in vacuo or in air for $\frac{3}{4}$ –1 hour. Among these are yttrotantalite, eschynite, brannerite, and some

euxenites, including a specimen of Simpson's (1951, pp. 257-259) tant-euxenite from Cooglegong, Pilbara Goldfield, Western Australia.²

However, kobeite from the type locality—Shiraishi, Kobe-mura, Kyoto Prefecture, Japan—gives x-ray patterns without being heated,

TABLE 3. INDEXING OF POWDER PATTERNS OF PARINGA RIVER MINERAL

<i>hkl</i>	A		B	
	Heated in air		Heated in vacuo	
	<i>d</i> , Å	<i>a</i> ₀	<i>d</i> , Å	<i>a</i> ₀
(111)	2.90	5.027	2.89	5.012
(200)	2.514	5.030	2.508	5.015
(220)	1.778	5.027	1.772	5.011
(311)	1.517	5.030	1.513	5.018
(222)	1.451	5.025	1.447	5.010
(400)	1.256	5.025	1.254	5.014
(331)	1.156	5.036	1.153	5.027
(420)	1.126	5.036	1.124	5.024
(422)	1.028	5.034	1.026	5.026
(511)	.968	5.029	.967	5.025
(440)	.890	5.032	.888	5.027
(531)	.850	5.028	.850	5.032
(600)	.838	5.027	.839	5.034

Exceedingly faint lines, one in A and two in B, that are not permitted by the space-group are omitted.

A. Average *a*₀ = 5.029 Å.

B. Average *a*₀ = 5.021 Å.

and after being heated in air or in vacuo, that are almost identical with those yielded by the Parínga River mineral under corresponding circumstances. This is doubly interesting since Takubo, Ukai, and Minato (1950, p. 511) have reported that after kobeite is heated to 900° C. for 30 minutes hardly any signs of recrystallization were evident when the mineral was subsequently examined optically and by x-ray diffraction methods. Unheated kobeite gives a weak pattern (Table 1, column *B*) that is identical with that yielded by the Parínga River mineral except for the presence of a few additional exceedingly faint, diffuse lines at

² Arnott (1950, pp. 389, 399) obtained a similar pattern for tanteuxenite from Eleys, Western Australia, but he does not record the temperature at which the specimen was heated, nor the length of time of heating. The present writer has determined that if tanteuxenite is heated in vacuo at 1200° C. for 1 hour a typical euxenite-type pattern (Arnott, 1950, pp. 396-397; Berman, 1955, pp. 817-818) is obtained by x-ray diffraction.

TABLE 4. X-RAY DIFFRACTION POWDER PATTERNS FOR PARINGA RIVER MATERIAL AND KOBITE, JAPAN

All specimens heated for 1 hour at 1200° C. Radiation $\text{CuK}\alpha=1.5418 \text{ \AA}$

A		B		C		D	
<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>
5.55	1	5.55	<1	5.46	<1	5.46	<1
4.15	1	4.13	<1	4.13	<1	4.13	<1
—	—	3.74	<1	3.71	<1	3.71	<1
3.59	1	—	—	3.61	<1	3.61	1
3.29	1	—	—	—	—	—	—
3.06	1	3.06	<1	3.07	<1	3.07	1
2.92	10	2.92	10	2.91	10	2.91	10
—	—	2.844 ¹	3	—	—	—	—
2.781	3	2.789	3	2.781	3	2.781	3
2.564	<1	—	—	—	—	—	—
2.501	4	2.500	4	2.500	4	2.495	4
2.417	<1	—	—	—	—	2.413	<1#
—	—	—	—	—	—	2.355	<1#
2.286	2	2.286	2	2.281	2	2.274	2
2.089	<1	—	—	2.084	<1	—	—
1.884	<1	—	—	—	—	1.880	<1
1.809	7	1.811	6	1.806	6	1.806	7
1.770	<1	1.770	<1	1.768	<1	1.767	<1
1.742	3	1.737	4	1.734	4	1.739	3
1.721	1	1.722	<1	1.715	<1	1.720	1
1.630	<1	—	—	—	—	1.630	<1
1.604	<1	—	—	—	—	1.606	<1
1.538	2	1.542	3	1.541	3	1.538	2
1.518	3	1.518	4	1.516	4	1.518	3
—	—	1.4955	<1	—	—	—	—
1.479	2#	1.472	2#	1.471	2#	1.476	2#
1.466	1#	—	—	—	—	1.467	1#
1.422	<1#	1.426	<1	—	—	—	—
1.330	<1	—	—	1.325	<1	—	—
1.255	2	1.256	2	1.254	2	1.254	2
1.174	2	1.175	2#	1.175	2#	1.174	2
—	—	1.159	<1	—	—	—	—
1.141	1	1.142	2#	1.141	2#	1.140	2
1.118	1	1.119	1#	1.117	1#	1.117	1#
1.109	1	1.105	1#	1.104	1#	1.106	1#
1.046	1	1.048	1#	1.046	1#	1.045	1#
1.031	1#	1.032	1#	1.033	1#	1.032	1#
.982	1	.981	1#	.981	1#	.980	1#
.970	1	.969	1#	.969	1#	.969	1#
.906	1	.906	<1#	.905	<1#	.905	1#
.865	1#	.864	1#	.865	1#	.865	1#
.852	<1#	.852	<1#	.852	<1#	.851	<1#
.840	<1#	.840	2#	.839	2#	.839	2#

¹ Not present in most films of Paranga River Material.

Diffuse line.

A. Kobeite, Japan, heated in vacuo.

B. Paranga River mineral heated in vacuo.

C. Paranga River mineral heated in air.

D. Kobeite, Japan, heated in air.

Additional lines are present in all films but it is not possible to measure them accurately owing to faintness and diffuseness.

higher 2θ values in the film of Japanese kobeite. At the same time another film of Japanese kobeite exhibits a few elongated spots that indicate a very slight degree of order; this is almost certainly due to remnants of the original structure.

Specimens of Japanese kobeite after being heated to 620°C . for 1 hour in air or in vacuo, on most occasions yield powder patterns that are identical to one another, and to the patterns found for the Paringa River mineral after being heated in air; a few spots were observed in one film. The heating of kobeite in air did not produce an increase in d -spacings over those found for this mineral after being heated in vacuo; in this it differs from the Paringa River mineral. Comparisons of the d -spacings of kobeite and of the Paringa River mineral, both heated to 620°C . are set out in Table 2.

X-ray diffraction powder patterns secured with both kobeite and the Paringa River mineral heated to 1200°C . in air or in vacuo are distinct from those yielded at the lower temperature and a glance at Table 4 makes it clear that there are no significant differences in these patterns of the high temperature modification. Although otherwise similar to the patterns found to be constant (Table 4) one fragment of the Paringa River material, after being heated in vacuo for 1 hour at 1200°C ., yielded an additional weak reflection at 2.844 \AA and the relative intensity of the line at 1.770 \AA is of the order of 2; in one other instance it is about 5, although the 2.844 \AA reflection is missing in this case. Furthermore, two fragments of Japanese kobeite after being heated in vacuo gave X-ray films with intensities of 2 for the reflection at or close to 1.770 \AA . This line appears to correspond with and result from the persistence of the relatively strong (220) reflection found in all films of these minerals that have been heated to the lower temperature of 620°C ., but it is not clear why it should persist more distinctly in some instances and be almost absent in most, unless this situation is connected with the apparent localization of radioactive material in the mineral, a condition that is clearly observed in the radiographs of the Paringa River mineral at least. In this connection it is of interest to compare the patterns obtained for these two minerals that had undergone heating at 900°C . for 30 minutes, the conditions under which Takubo *et al.* (1950, p. 511) found no significant recrystallization had resulted in kobeite. In these films (Table 5) the uraninite-type pattern is dominant but with the strongest lines of the unique higher temperature phase or phases also present, so that the reflection close to 1.770 \AA is much more intense than those immediately on either side of it. It is interesting to observe that the reflection at approximately 4.15 \AA is the only line that persists in films yielded by

TABLE 5. COMPARISON OF X-RAY DIFFRACTION PATTERNS YIELDED BY KOBITE, JAPAN, AFTER FRAGMENTS HAD BEEN SUBJECTED TO TEMPERATURES OF 620° C. (A), 900° C., (B), AND 1200° C. (C) IN VACUO

Radiation $\text{CuK}\alpha=1.5418 \text{ \AA}$. Intensities determined visually

A		B		C	
<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>	<i>d.</i> meas. \AA	<i>I</i>
—	—	5.94	<1	—	—
—	—	—	—	5.55	1
—	—	4.45	1	—	—
4.15	1	4.15	<1	4.15	1
3.76	<1	3.76	<1	—	—
—	—	3.56	<1	3.59	1
—	—	3.34	1	3.29	1
—	—	3.25	<1	—	—
—	—	—	—	3.06	1
2.89	10	2.92	10	2.92	10
—	—	2.82	1	2.781	3
—	—	—	—	2.564	<1
2.505	4	2.515	7	2.501	4
—	—	—	—	2.417	<1
—	—	2.284	<1	2.286	2
—	—	2.073	<1	2.089	<1
—	—	1.912	1	—	—
—	—	—	—	1.884	<1
—	—	1.808	3	1.809	7
1.777	8	1.782	5	1.770	<1
—	—	1.744	1	1.742	3
—	—	1.720	<1	1.721	1
—	—	1.627	<1	1.630	<1
—	—	—	—	1.604	<1
—	—	1.538	<1	1.538	2
1.516	7	1.520	6	1.518	3
—	—	—	—	1.479	2#
—	—	—	—	1.466	1#
1.453	1	—	—	—	—
—	—	—	—	1.422	<1#
—	—	1.368	<1	—	—
—	—	—	—	1.330	<1
1.255	1	1.255	2	1.255	2
—	—	1.176	1	1.174	2
1.154	2#	1.141	<1	1.141	1
1.125	2#	1.129	1	1.118	1
—	—	—	—	1.109	1
—	—	1.046	<1	1.046	1
1.028	1#	1.032	2#	1.031	1#
—	—	.979	1#	.982	1
.969	1#	.970	1#	.970	1
—	—	—	—	.906	1
—	—	.864	2#	.865	1#
.851	<1#	.852	2#	.852	<1#
.838	2#	.839	3#	.840	<1#

Diffuse lines.

unheated material and material heated at 620° C., 900° C., 1000° C., and 1200° C.; and furthermore it remains very weak throughout. After being heated to this intermediate temperature of 900° C. particle size is still quite minute as evidenced by broadness or diffuseness of most lines.

The temperature of 1200° C. was chosen because work in progress in connection with a wide variety of multiple oxides of tantalum, niobium, and titanium has shown that this temperature is a convenient one in most instances if reproducible *x*-ray diffraction patterns are to be obtained. However, subsequent experiments with kobeite and the Paringa River mineral have shown that heating to 1000° C. for 40 minutes will give identical and reproducible results.

NOMENCLATURE

The *x*-ray diffraction study of the Paringa River material before and after heat-treatment clearly suggests that this mineral is identical, or at least very closely related to, kobeite from Japan described by Takubo *et al.* (1950), but apparently distinct from a number of other multiple oxides of tantalum, niobium, and titanium. The actual appearance of the two minerals in their host rocks is strikingly similar, although the Paringa River mineral exhibits no pronounced alteration to an anatase-rich product; this may be due to a difference in age. Finally the chemical data, although less complete than the physical, do not detract from this similarity. Therefore it is believed that the Paringa River mineral is kobeite, and it is hoped that it will be found *in situ* and more and better material obtained that will allow a more thorough study than that reported here.

Study of the Japanese report at first leads one to the conclusion that kobeite might be a high-titanium member of the euxenite-polycrase or eschynite-priorite groups, but eight specimens that undoubtedly belong to one or other of these groups yielded *x*-ray patterns after being heated to 1200° C. that exhibited little if any resemblance to patterns obtained with kobeite similarly treated; the same observation may also be made for fergusonite, including risörite, brannerite, samarskite, and yttrotantalite. These data rather definitely support the suggestion that kio-beite is a distinct and valid mineral species, and it is hoped that the results of work in progress in connection with a number of multiple oxides of tantalum, niobium, and titanium, may provide further data on this question.

SOURCE

Granitic intrusions and pegmatites are known to outcrop at many localities in the general area from which the kobeite-bearing rock was obtained, but so far as the writer is aware no tantalum-niobium bearing

minerals have been found in these rocks. However, it might be pointed out that tantalum cassiterite is not a rarity in concentrates from sands and gravels in many localities in Westland (Hutton, 1950). Again radioactive minerals such as uranoan thorite, huttonite, monazite, xenotime, and others (Hutton, 1950) have been found in South Westland sands and gravels, although the actual source for these minerals has not been determined as yet. The problem of the source of kobeite is complicated further by the existence of large quantities of glacial debris, much of which has been resorted by rivers and streams.

ACKNOWLEDGMENTS

I wish to acknowledge the opportunities provided for this research by the award of a John Simon Guggenheim Foundation Fellowship. To Dr. T. Minato of Kyoto University, Japan, I am most grateful for his kindness in sending me specimens of kobeite from the type locality, and I am much indebted to my friend Mr. Yoshihiko Shimazaki for his full and careful translation of the paper on kobeite by Takubo, Ukai, and Minato. A grant from the University Committee on Supplementary Research Grants permitted the purchase of special high-silica tube and other items; this assistance was much appreciated.

REFERENCES

- ARNOTT, R. J. (1950), X-ray diffraction data on some radioactive oxide minerals: *Am. Mineral.*, **35**, 386-400.
- BERMAN, J. (1955), Identification of metamict minerals by x-ray diffraction: *Am. Mineral.*, **40**, 805-827.
- HUTTON, C. O. (1950), Studies of heavy detrital minerals: *Geol. Soc. Am. Bull.*, **61**, 635-716.
- (1951), Allanite from Yosemite National Park, Tuolumne Co., California: *Am. Mineral.*, **36**, 233-248.
- MARBLE, J. P. (1948), Some applications of autoradiography: *Intern. Geol. Congress, Rept. 18th Session, Gt. Britain*, Pt. II, pp. 80-85.
- SIMPSON, E. S. (1951), Minerals of Western Australia, 2nd. vol., esp. pp. 257-261, Govt. Printer, Perth, Western Australia.
- SWANSON, H. E., AND TATGE, E. (1953), Standard x-ray diffraction patterns: *Nat. Bur. Standards Circ.*, **539**, Vol. I.
- TAKUBO, J., UKAI, Y., AND MINATO, T. (1950), Studies on the minerals containing rare elements (Part II); Kobeite from Shiraishi, Kobe-mura, Nakagun, Kyoto Prefecture: *Journ. Geol. Japan*, **56**, 663, 509-513 (in Japanese).

Manuscript received Aug. 31, 1956.

A SPECTROGRAPHIC STUDY OF THE MINOR ELEMENT CONTENT OF DIAMOND

F. A. RAAL, *Diamond Research Laboratory, Johannesburg, South Africa.*

ABSTRACT

A rapid spectrographic method for the quantitative assessment of trace element constituents in diamond is described. Of the fourteen elements looked for in twenty-five diamond specimens only eight made their appearance, with Si, Mg, Al, Ca, Fe and Cu the most important.

The color of diamond is linked, at least in part, with the presence of Fe and Cu. Type I diamonds are found, in general, to be more impure than Type II diamonds. Very little difference is observed as regards the nature and amounts of the impurities in Types IIa and IIb diamonds.

INTRODUCTION

It has long been a subject of considerable interest as to what minor elements, if any, are contained in diamond and to what extent these impurities are responsible for the color of diamonds, fluorescence, semi-conductivity, etc.

Unfortunately, very little work has been done in this connection up to the present and of the few incompressive references existing in the literature, only that of Chesley (1) is of any significance. No work, from a quantitative point of view, has been reported. This lack of information must be attributed to the difficulty of obtaining diamond specimens for research purposes, especially in view of the fact that the stones have to be partially destroyed in order to glean the required information.

The Diamond Research Laboratory has devoted much time to diamond analysis on a quantitative basis and has developed a method which, besides obviating time consuming measurements, has proved to be very satisfactory.

EXPERIMENTAL PROCEDURE

The first requirement is for standard mixtures to be made up in order to establish working curves whereby the respective amounts of the trace constituents can be assessed. In these standards it is essential to introduce an internal standard since its presence constitutes the basis of our analysis. This internal standard is some suitable element or compound, added to the standards or diamond samples to be analyzed in a fixed proportion, so that a relationship between the densities of selected spectral lines of this element and those of the elements being determined can be established. The presence of the internal standard furthermore permits spectra of the standards and the diamond samples to be carried on different plates, and source variations, etc., can be readily compensated for. Cobaltous oxide is found to be very suitable.

To prepare the strongest standard, 0.1 gm. of the summation weight of a mixture of elements most likely to be present in diamond is mixed with pre-determined weights of exceptionally pure Johnson, Matthey & Co., Ltd., Cat. No. *JM 2B* graphite power and cobaltous oxide to result in a standard containing 1% of each trace element constituent and 5% cobaltous oxide as internal standard.

From this 1% standard, subsequent dilutions with the base (*JM 2B* graphite powder with 5% admixed cobaltous oxide) are made in steps of $1:\sqrt{10}$, i.e. 0.316 gm. of each mixture is diluted with 0.684 gm. base (2). In this way a series of standard mixtures is obtained having graphite as matrix material and containing each individual trace element in amounts of 10,000 parts per million, 3160 p.p.m., etc., down to 1 p.p.m.

A 3.5 mg. portion of each standard is carefully weighed out and mixed with its own weight of pure graphite powder, and the whole used to fill the cavity in the specially shaped cathode shown in Fig. 1. This cathode

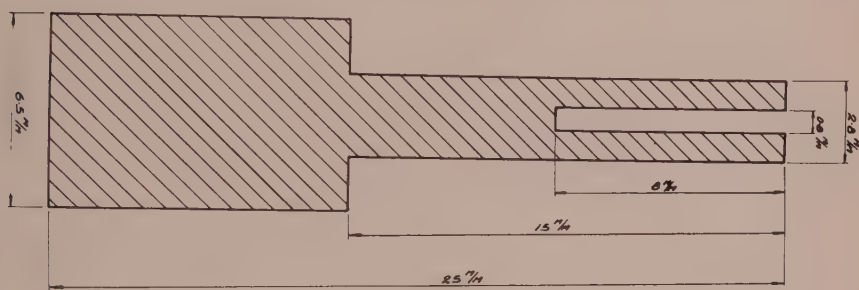


FIG. 1

has been advocated by various investigators such as Mitchell (2), and has proved most successful. It is shaped from pure *JM 2B* graphite rod 6.5 mm. in diameter, 25 mm. long and reduced in diameter over the upper 15 mm. to 2.8 mm. The boring is 0.8 mm. in diameter, and 8 mm. deep and can be filled expeditiously by slipping a tight fitting cellophane collar over the narrow portion of the electrode. A length of the same 6.5 mm. graphite rod is used as anode.

The spectrograph in use is the Hilger Model *E.492*. A 150 volt D.C. source with variable resistance and inductance in series is used for excitation purposes. The samples are ignited at a current of 6 ± 0.3 amps and an electrode separation of 5 mm. A slit width of 0.01 mm., slit height of 8 mm. and shutter aperture of 8 mm. are found advantageous. Following the cathode layer arc technique (2) exposures are made in the 3175–8000 A.U. and 2380–3290 A.U. ranges for 120 secs. and 180

secs. respectively on Ilford Thin Film Half Tone Plates and the same development procedure strictly adhered to throughout, *i.e.* $4\frac{1}{2}$ minutes in *I.D.* 2 metol-hydroquinone developer at full strength and a temperature of 18° C.

The most persistent lines of the various elements are easily identified and the ones selected for analysis are listed in Table 1.

TABLE 1

Element sought	Analysis line in A.U.	Element sought	Analysis line in A.U.
Aluminium Al	3092.7	Magnesium Mg	2852.1
Barium Ba	4554.0	Nickel Ni	3619.4
Calcium Ca	3179.3	Silicon Si	2516.1
Chromium Cr	4254.3	Silver Ag	3280.7
Copper Cu	3274.0	Sodium Na	3302.9
Iron Fe	2599.4	Strontium Sr	4607.3
Lead Pb	2833.1	Titanium Ti	3349.4

The densities of these lines for the various different concentrations of the standards are then carefully recorded by means of a Kipp recording microphotometer. The density of a line is taken as the logarithm of the opacity which, in turn, is defined as the ratio of the intensity of the light transmitted by the clear plate (I_0) to that transmitted by the line image (I). The value of I_0 is taken each time as the mean of several readings on both sides and close to the line to be measured. This procedure eliminates the need of background correction since the ratio of the galvanometer deflection obtained for line and background and background images gives, in fact, a value for the transmission of the line freed from background.

A plot of the densities measured in the above way as a function of the logarithm of the concentration provides our standard working curves.

It should be noted that the line densities and therefore the working curves of the different elements are obtained relative to the line densities of the cobalt 2663.5 and 3334.1 A.U. lines. With due care to experimental procedure the line densities of the latter exhibit remarkable constancy for the different exposures thereby indicating the absence of excessive source and other fluctuations.

To ascertain the amounts of trace constituents in diamond, a spectrogram is made of the stone as far as possible under precisely the same conditions as the standards. Since only a small piece of diamond is necessary for spectrum analysis, the general procedure adopted is to saw or cleave

the diamond so as to provide two end pieces of approximately 50 mg. each and a middle piece, which on polishing, results in a specimen with optically parallel windows. This middle piece is then used for light absorption measurements with a *Model DU* Beckman spectrophotometer over the range 2000–10000 A.U. In this way it can be ascertained to what type the diamond belongs. The diamond type has been designated according to the following criterion.

Type II diamonds are transparent to about 2250 A.U. (3). This class of diamond has been further subdivided into Types II*a* and II*b* (4). Type II*b* diamonds are in general blue, and this color arises out of absorption lines in the near infra-red (5). They conduct electricity and behave as *p*-type semi-conductors (6). Type II*a* diamonds do not show these infra-red absorption lines and are non-conductors.

Type I diamonds show a secondary absorption edge at about 3200 A.U. The strength of this edge varies with the number of group *A* centers present which absorb at this wave length (5). The number of these centers may be assessed, in a qualitative way, from the wave length limit of transmission as measured on the spectrophotometer. Thus, in Table 2, we define:

Transmission limit equal to or larger than 3000 A.U.—Extreme Type I.

Transmission limit between 2800–3000 A.U.—Medium Type I.

Transmission limit between 2400–2800 A.U.—Weak Type I or Mixed Type.

Transmission limit between 2250–2400 A.U.—Type II.

The end pieces of the diamond are subjected to rigorous cleaning, first in “aqua regia” and then chromic acid at mild heat to remove all traces of surface impurities. The pieces are then transferred to a small impact crusher which has been buffed clean beforehand on an iron wheel, and are shattered by one sharp blow with a hammer.

The resulting powder is treated with 50% nitric acid followed by further treatment with 50% hydrochloric acid solution. It is washed by decantation with distilled water until completely free from chloride and dried at about 100°C.

A 3.5 mg. portion of the diamond powder is weighed out and mixed with its own weight of base, which was specified under the heading “Experimental Procedure.” Spectrograms of this mixture are obtained under the same conditions as those prevailing with the standards. Lines due to trace constituents, if any, are identified and the densities measured. Before assessing the amounts of constituents present the densities of the Cobalt 2663.5 and 3334.1 A.U. lines are first measured and compared with those of the working curves. If different, the line densities of the constituent elements are adjusted in accordance with this difference

before interpolations are made on the working curves. In general, it is found that with due care in the duplication of experimental procedure, the densities of the reference cobalt lines do not show appreciable deviations from the standard values. This is a condition to be aimed at since the unknowns in the diamond might respond differently than the internal standard to voltage and current variations.

GEOGRAPHIC LOCATION AND COLOR OF STONES

In all, twenty-five diamonds were studied. Two of these, Nos. 1 and 2, came from Sierra Leone. No. 1 was colored a green-yellow whereas No. 2 had a pale green color.

Thirteen diamonds, Nos. 3–15, came from the Premier Mine, South Africa. Stones 3–8 were a natural blue and of the Type II*b* variety, while Nos. 9–15 were all colored various shades of brown. Of the brown variety three diamonds, Nos. 9–11, were of Type II*a* while the rest, Nos. 12–15, belonged to the Type I classification.

Six diamonds, Nos. 16–21, were of a fine yellow color and originated from the Consolidated Diamond Mines in South West Africa.

Of the remainder, No. 22 was a white Type II*a* diamond from the Wesselton Mine, South Africa, No. 23 white, and Nos. 24 and 25 brown. Unfortunately, the sources of origin of the last three diamonds are not known.

RESULTS AND DISCUSSION

Quantitative spectrographical analysis is never an easy procedure and with diamond in particular it proves to be even more difficult, due to the nature of the material and the fact that the trace constituents are present to the extent of a few parts per million only. It is of essence, therefore, to be extremely meticulous in the handling and preparing of the samples, the conditions of exposure, etc., in order to get anything like reproducible results.

Quite often good duplication of results was found for duplicate samples and only four exposures were necessary, *i.e.*, two in the lower wave length bracket and two in the higher.

Sometimes, however, it was necessary to take some eight exposures of samples of the same diamond before any reliable duplication could be obtained. These contradictory findings could be due to minute inclusions in the diamond or it might well be that the impurities in diamond are localized and not uniformly distributed throughout the crystal. Berman, *et al.* (7) in their work on the thermal conductivity of diamond arrived at the conclusion that imperfections in diamond, the nature of which is not specified, occur in groups.

The results of the investigation are given in Table 2, together with

TABLE 2

Diamond No.	Geographic Location	Color	Type	P.P.M. of								Special Effects
				Si	Ca	Mg	Al	Fe	Ti	Cu	Cr	
1	Sierra-Leone	Green-yellow	Medium I	4 2	5 4	4 4	56 58	20 15	4 4	7 6	a a	BF
2	Sierra-Leone	Pale green	Medium I	3 2	1 2	3 2	3 16	10 17	4 5	7 10	trace a	BF
3	Premier	Natural blue	II(b)	4 2	a 3	1 32	34 a	a a	a a	a a	a a	P, S-C
4	Premier	Natural blue	II(b)	2 4	a a	2 2	8 6	a a	a a	a a	a a	P, S-C
5	Premier	Natural blue	II(b)	4	a	4	10	a	a	a	a	P, S-C
6	Premier	Natural blue	II(b)	2 1	a a	4 3	4 3	1 2	a a	a a	a a	P, S-C
7	Premier	Natural blue	II(b)	1 2	a a	5 7	7 4	a a	a a	a a	a a	P, S-C
8	Premier	Natural blue	II(b)	1 2	a a	2 2	3 2	a a	a a	a a	a a	P, S-C
9	Premier	Brown	II(a)	2 2	a a	3 2	4 1	a a	a a	a a	a a	—
10	Premier	Brown	II(a)	5 10	a a	10 5	10 13	a a	a a	a a	a a	—
11	Premier	Brown	II(a)	a 1	a a	3 5	1 2	a 1	a a	2 a	a a	—
12	Premier	Brown	Medium I	6 3	20 6	3 2	4 10	9 13	8 7	6 6	a a	BF
13	Premier	Brown	Extreme I	51 7	15 7	15 5	79 47	10 13	a 3	3 4	a a	BF, Z
14	Premier	Light brown	Medium I	2 2	2 6	6 9	10 2	a 2	4 3	6 2	a a	BF, Z
15	Premier	Light brown	Medium I	1 3	a 2	3 4	9 10	24 29	4 3	5 a	a a	GF, Z
16	S.W.A.	Fine yellow	Extreme I	2 a	5 3	8 2	25 19	15 8	a 3	3 4	a a	YF
17	S.W.A.	Fine yellow	Extreme I	2 1	2 a	4 2	8 3	9 4	a 1	3 2	a a	BF
18	S.W.A.	Fine yellow	Weak I (Mixed?)	a a	a a	2 2	1 1	12 7	a a	3 4	a a	YF, Z
19	S.W.A.	Fine yellow	Extreme I	a a	a a	1 2	8 8	12 20	a a	2 a	a a	YF
20	S.W.A.	Fine yellow	Extreme I	1 a	4 6	a 3	13 10	12 18	a a	5 3	a a	YF
21	S.W.A.	Fine yellow	Extreme I	1 5	2 4	1 3	2 9	8 17	a a	4 2	a a	YF
22	Wesselton	White	II(a)	a a	2 2	1 1	4 3	a a	a a	a a	a a	—
23	Unknown	White	Medium I	a a	a a	2 2	10 2	a a	a a	2 2	a a	BF
24	Unknown	Brown	Medium I	1 1	2 2	4 1	6 3	10 16	1 2	a a	a a	BF, Z
25	Unknown	Mottled brown	Medium I	1 a	a a	4 3	a a	4 1	a a	5 3	a a	GF

BF = Blue fluorescence.
 GF = Green fluorescence.
 YF = Yellow fluorescence.
 P = Phosphorescence.

S-C = Semi-conducting.
 Z = Zoned i.e. fluorescence not uniform throughout the diamond but restricted to localized spots or zones.

P.P.M. = Parts per million
 a = Absent (not detectable)

special effects such as semi-conductivity, fluorescence etc., observed for each diamond. Except for diamond No. 5 where the specimen was too small to permit duplication, the results are given in duplicate.

Of the fourteen elements looked for, only Si, Ca, Mg, Al, Fe, Ti, Cu and Cr made their appearance, with Ag, Ni, Pb, Na, Ba and Sr absent in all cases. However, the failure to detect these elements does not rule out their presence altogether. The limits of detection of some of these elements, notably Pb and Ba, are of the order of anything up to 10 p.p.m. and they might be present to an extent such that the most persistent lines are not detectable.

The presence of Co could of necessity not be established since it is used as the internal standard.

The main impurities in diamond seem to be Si, Ca, Mg, Al, Fe and Cu, with the Al predominating in most cases. This result is not surprising since the first five elements are found abundantly in nature and are readily detectable by the spectrograph.

The colored diamonds, *i.e.*, the South West African yellows, the two Sierra Leone stones and the brown diamonds with the exception of the IIa diamonds all contain Fe, up to an appreciable amount in some cases. Cu also shows a tendency to be present in the colored stones with the exception of the IIa diamonds again. Ti appears only when Fe is present. The theory of Sutherland and co-workers (8) to the effect that Type I diamonds are more impure than Type II diamonds seems, in general, to have credence although there are exceptions. Thus medium Type I diamond No. 23 has a total impurity content of 6–14 p.p.m. whereas Type IIa diamond No. 10 contains 25–28 p.p.m.

On the whole, Type IIa and IIb diamonds appear to differ very little as regards impurity content. The impurities are, almost exclusively, Si, Mg, and Al with the latter predominant in most cases.

A current theory is that Al, by virtue of its being an electron-acceptor is, at least in part, responsible for the semi-conducting properties of Type IIb diamonds. If this is the case the Al in Type IIb diamonds may be accommodated differently in this type of diamond than in Type IIa diamonds, since the amounts of Al are virtually the same in the two types. Alternatively, an excess of donor levels in Type IIa diamonds may "quench" the *p*-type semi-conductivity.

Finally, although it is apparent from the results that impurities in diamond have an effect on the color it is by no means an established fact that they constitute the main contributing factors for the anomalous light absorption of diamond in the ultra-violet and infra-red, semi-conductivity, etc.

It looks rather at this stage as if impurities in conjunction with defects inherent in the diamond are responsible for these observed phenomena.

ACKNOWLEDGMENTS

The author wishes to thank Messrs. Industrial Distributors (1946) Limited for providing the diamonds and for permission to publish this paper. The author is also indebted to Dr. J. F. H. Custers, Director of Research, for his continuous interest and advice and to Mr. I. H. D. Lund for his valuable assistance.

REFERENCES

1. CHESLEY, F. G. (1942), *Am. Mineral.* **27**, 20.
2. MITCHELL, R. L., (1948), The spectrographic analysis of soils, plants and related materials: *Commonwealth Bureau of Soil Science Technical Communication No. 44*.
3. ROBERTSON, R., FOX J. J., AND MARTIN, A. E. (1933), *Phil. Trans. Roy Soc. (London)*, A, **232**, 463.
4. CUSTERS, J. F. H. (1952), *Physica*, **18**, 489.
5. CLARK, C. D., DITCHBURN, R. W., AND DYER, H. B., (1956), *Proc. Royal Soc.*, A, **234**, 363.
6. CUSTERS, J. F. H. (1954), *Physica*, **20**, 183; *Nature*, London, **176**, 173 (1955).
LEIVO, W. J., AND SCHMOLUCKOWSKI, R., (1955), *Phys. Rev.*, **98**, 1532.
BROPHY, J. J. (1955), *Phys. Rev.*, **99**, 1336.
AUSTIN, I. G., AND WOLFE, R. (1956), *Proc. Phys. Soc.*, B, **69**, 329.
DYER, H. B., AND WEDEPOHL, P. T., (1956), *Proc. Phys. Soc.*, B, **69**, 410.
7. BERMAN, R., SIMON, F. E., AND ZIMAN, J. M. (1953), *Proc. Royal Soc.*, A, **220**, 171.
8. SUTHERLAND, G. B. B. M., BLACKWELL, D. E., AND SIMERAL, W. G. (1954), *Nature*, **174**, 901.

Manuscript received July 31, 1956

THE GRINDING HARDNESS OF DIAMOND IN A PRINCIPAL CUTTING DIRECTION*

REYNOLDS M. DENNING, *University of Michigan, Ann Arbor, Michigan.*

ABSTRACT

A series of facets in zone [010] was ground on a diamond. The grinding direction was maintained parallel to the zone axis, and the cutting rates were determined. It is shown that the grinding hardness of diamond even along a principal (four-fold) axis is dependent upon the orientation of the surface on which the measurement is made.

It is not possible to represent a grinding hardness solid, analogous, for example, with the optical indicatrix of transparent crystals. The implication is that if it were possible to develop a theory of grinding hardness in diamond, the simplest hardness model must be represented by a tensor of at least fourth order.

The purpose of the present note is to demonstrate that the grinding hardness of diamond, even parallel to a principal (four-fold) axis, is dependent upon the orientation of the surface on which the measurement is made. Grinding hardness is considered reciprocal to the rate of removal of material by grinding. It is fairly easy to demonstrate such a relationship for the more randomly located cutting directions. In the case of a four-fold symmetry axis the relatively easy grinding along such a direction in any plane makes the measurement rather difficult. The preliminary data presented in a previous paper (Denning, 1955) are not sufficiently exact to warrant positive conclusions for so special a direction as the one under consideration. Such uncertainty exists because the measurements were made at widely separated times, which necessitated unavoidable systematic errors in the grinding rate of the reference standard. In that work the hardness data for various grinding directions on a given surface are consistent with each other, but a comparison of hardness from one surface to another is only approximately valid.

In the present study measurements were made simultaneously on two diamonds, one ground on (001) along [010] as a reference, the other on a series of planes in zone [010]. The cutting direction on the latter diamond was maintained in the [010] direction. The relative grinding hardness was determined for each of these planes. The relative grinding hardness along [010] is the same in either direction, since this direction is normal to a symmetry plane. If, however, the surface on which the measurement is made is not quite normal to the symmetry plane (010), then an appreciable asymmetry of grinding rates is introduced. For example, if a plane whose two-circle coordinates are $\phi = 90^\circ$, $\rho = 1^\circ$ is ground toward (100) and then toward ($\bar{1}00$), then toward (010) and

* Contribution from the Department of Mineralogy and Petrography, University of Michigan, No. 213.

($0\bar{1}0$), and the results are compared with those from a surface exactly parallel with (001), ground in analogous directions, it is found that the measurements in the first case ($\phi = 90^\circ$, $\rho = 1^\circ$) toward ($\bar{1}00$) show appreciably greater hardness than the other three sets of measurements. The latter three all exhibit about the same hardness as the four analogous directions on a plane accurately parallel to (001). In practice, at least with the methods here employed, it is impossible to orient planes with an accuracy of much better than 15 minutes of arc. In order to minimize orientation errors the planes studied were oriented to a tolerance of $+0'$, $-30'$ from parallel to [010]. That is, the orientation error was kept toward the soft, rather than the hard, direction. In this way a valid average of cutting rate can be obtained. Such an average could not be used if the surface were located to $\pm 15'$. The accuracy of the ρ angle is of no particular importance because of the small rate of change of relative grinding hardness with respect to this angle. Special care has been taken to minimize systematic errors. The areas of the facets have been kept constant to within a factor of two. The shapes of the facets were nearly identical in all tests except one. The lowest value of relative grinding hardness was determined on ($00\bar{1}$) on an elongated facet whose length was perpendicular to the grinding direction. Such an orientation of a rectangular face favors a more rapid rate of removal of material than an equidimensional surface of the same area because more abrasive is available for cutting. The low hardness value thus obtained was omitted in plotting the accompanying curve.

Table 1 is a summary of the data obtained from 14 facets. Each hardness value is the average of three independent determinations. The last column is an average of the four quadrants according to the symmetry and adjusted to unit hardness for the reference direction. Figure 1 shows the appearance of an octahedron on which the first nine facets of Table 1 are drawn. The length of the arrows is proportional to the relative grinding hardness in the direction of the arrows. In Fig. 2 the dependence of hardness along [010] for the series of planes is given. The curve is idealized, but the original data points are included. The validity of averaging these quadrants has been established from other measurements which involve a greater hardness variation than those under consideration (Wilks & Wilks, 1954; Denning, 1955). A statistical examination of the data removes any doubt of the reality of the difference in relative grinding hardness on the optimum grinding direction of the cube and dodecahedron.

The optimum cutting direction on the dodecahedron is slightly softer than the same direction on a cube facet. The magnitude of the observed hardness variation is not very great. To the practical cutter or user of

TABLE 1. RELATIVE GRINDING HARDNESS OF DIAMOND ALONG [010] ON A SERIES OF PLANES. (THE SECOND DECIMAL PLACE IS NOT SIGNIFICANT)

Facet Number		ϕ	ρ	Average Hardness	Adjusted Hardness
1	cube (001) dodecahedron (101)	—	0°	1.03	1.00
2		90°	11°	0.81	0.83
3		90°	23°	0.68	0.62
4		90°	36°	0.43	0.52
5		90°	45°	0.59	0.51
6		90°	51°	0.58	0.51
7		90°	59°	0.59	0.56
8		90°	74°	0.49	0.64
9		90°	90°	1.21	1.00
10	dodecahedron (10 $\bar{1}$)	90°	135°	0.48	0.51
11	cube (00 $\bar{1}$)	—	180°	1.14	1.00
12	dodecahedron ($\bar{1}$ 0 $\bar{1}$)	270°	135°	0.46	0.51
13	cube ($\bar{1}$ 00)	270°	90°	0.73	1.00
14	dodecahedron ($\bar{1}$ 01)	270°	45°	0.56	0.51

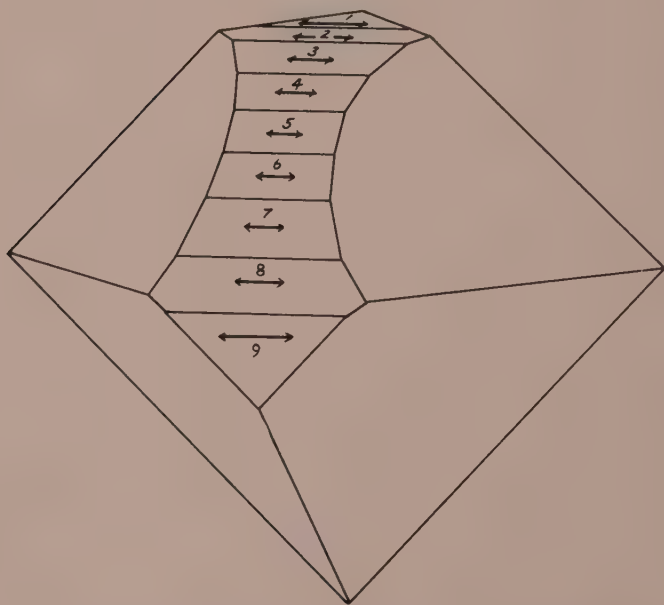


FIG. 1. Relative grinding hardness vectors parallel to [010].

diamonds, the hardness variation along a four-fold symmetry axis is negligible. Such variation may be of theoretical interest in the detailed interpretation of the relation of the diamond structure to directional hardness variation.

It is of interest to note that to specify fully the continuous grinding

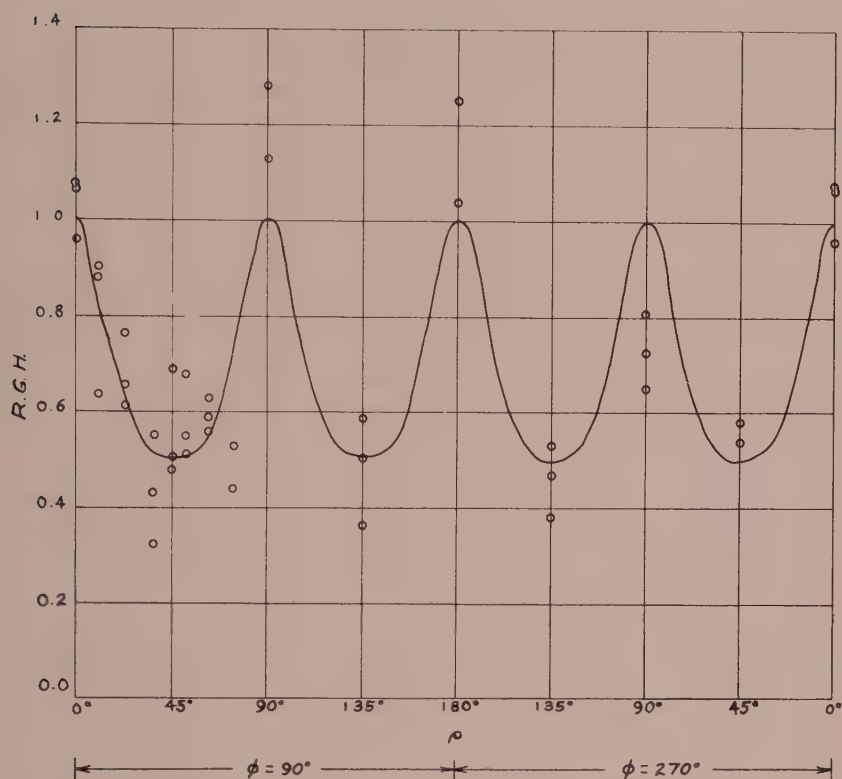


FIG. 2. Relative grinding hardness of diamond along [010]. The curve is averaged according to the four-fold symmetry of this direction. The values along the abscissa are the two-circle coordinates of the facets on which the hardness was measured.

hardness values of a crystal, the hardness values must be plotted against three dimensions. Two of these may designate the orientation of the grinding direction (or plane being ground) and the third, the position of the plane on which measurements are made (or azimuth of grinding direction on the plane). For this reason it is not possible to construct a grinding hardness solid, analogous, for example, with the optical indicatrix of transparent crystals. The implication is that if it were possible

to develop a theory of grinding hardness in diamond, the simplest hardness model must be represented by a tensor of at least fourth order. It might seem that since a factor of two of hardness variation is not very great, that such a refinement is needed only if the higher order effects are to be explained. As more general directions are studied, the dependence of hardness in a given direction upon plane orientation is strikingly large. Actually such a relationship is implicit in the results of the hardness measurements in various azimuths on selected planes.

The writer acknowledges his thanks to Mr. Donald Hausen, who painstakingly made the hardness measurements. This investigation was supported by the Crystal Hardness project of the Office of Naval Research. The diamonds were contributed by Industrial Distributors, Ltd., of Johannesburg.

REFERENCES

- DENNING, R. M., Directional grinding hardness in diamond: A further study: *Am. Mineral.*, **40**, 186-191 (1955).
WILKS, E. M., AND WILKS, J., The hardness properties of cube faces of diamond: *Phil. Mag.*, ser. 7, **45**, 844-849 (1954).

Manuscript received Oct. 22, 1956.

URANIUM AND THORIUM IN THE ACCESSORY ALLANITE OF IGNEOUS ROCKS¹

WILLIAM LEE SMITH,² MONA L. FRANCK,³ AND ALEXANDER M. SHERWOOD, *U. S. Geological Survey, Washington 25, D.C.*

ABSTRACT

Accessory allanite was separated from phanocrystalline igneous rocks and its optical properties and radioactive components were compared. The indices of refraction of these allanite samples are higher than those from the pegmatites that are usually described in geologic literature. The birefringence was found to range from 0.015 to 0.021, the α -index of refraction from 1.690 to 1.775. The allanite content ranges from 0.005 to 0.25 per cent by weight in the rocks studied. The mineral is confined largely to the more siliceous phanerites. The uranium content is highest in the allanite from the granites sampled, ranging from 0.004 to 0.066 per cent, whereas the thorium content is high or low regionally, ranging from 0.35 to 2.33 per cent. Allanite was found to be otherwise of exceptionally uniform composition.

INTRODUCTION

Allanite, $(\text{RE},^*\text{Ca})_2(\text{Fe},\text{Al})_3\text{Si}_3\text{O}_{12}(\text{OH})$, may occur as an accessory mineral in siliceous and intermediate igneous rocks, in limestone contact skarns, pegmatites, crystalline metamorphic rocks, and as a component of magmatic iron ores. The mineral is monoclinic and varies in color from light brown to black. Its hardness ranges from 5 to 6 depending upon its degree of alteration, and similarly its specific gravity varies from 3.4 to 4.2. Allanite is a member of the epidote group with rare earths substituting for calcium. Allanite is often found with epidote; some of it is intergrown with epidote (Hobbs, 1889). The metamictization of allanite produces an amorphous alteration product, and some allanite from pegmatite is completely isotropic. The alteration is inferred to be the result of the destruction of the crystalline structure of allanite by the radioactive decay of its uranium and thorium.

MINERALOGY

Separation methods

In the granitic rocks that were studied, allanite was found to average 0.1 mm. in diameter. The rocks were pulverized on a roll-type crusher which liberated the allanite cleanly. The allanite was generally found to concentrate in the 100- to 200-mesh size fraction. Allanite concentrates

* Rare earths.

¹ Publication authorized by the Director, U. S. Geological Survey.

² Present address: Minerals Beneficiation Div., Battelle Memorial Institute, Columbus, Ohio.

³ Present address: Ferro Corp., Technical Service Lab., Cleveland, Ohio.

with the other accessory minerals in the sink of a methylene iodide separation (sp. gr. 3.33). It is easily separable from the other heavy minerals in a Frantz Isodynamic magnetic separator, allanite becoming magnetic between 0.4 and 0.6 amp. at cross and longitudinal settings of 10° . When epidote occurs with allanite, the separation becomes more difficult. The epidote floated and the allanite sank in methylene iodide saturated with iodoform (sp. gr. 3.45). Thus a minimum of hand-picking was required to obtain clean separates of the minerals.

Optical properties

All of the allanite studied was optically negative. The indices of refraction of the allanite were generally higher than those described in literature. This may be because the minerals generally described are the more metamict varieties from pegmatites. It is likely that the allanite described here is more abundant and more typical of the fresh mineral than the larger specimens obtained from pegmatites.

The optical data in Table 1 show that the α indices range from 1.690 to 1.775, β from 1.70 to 1.789, and γ from 1.706 to 1.791 with a possible error of ± 0.002 . Allanite is reported to have indices as low as n 1.60

TABLE 1. INDICES OF REFRACTION OF ALLANITE FROM IGNEOUS ROCKS

Host rock	α	β	γ	Birefringence
Southern California batholith				
<i>Coarse phase</i>				
Granite from Rubidoux Mountain, Riverside	1.775	1.789	1.791	0.016
<i>Fine Phase</i>				
Granite from Rubidoux Mountain, Riverside	1.735	1.750	1.752	0.017
Woodson Mountain granodiorite, Descanso	1.745	1.760	1.763	0.018
Woodson Mountain granodiorite, Temecula	1.735	1.750	1.753	0.018
Woodson Mountain granodiorite, Rainbow	1.740	1.755	1.759	0.019
Woodson Mountain granodiorite, Elsinore	1.740	1.755	1.760	0.020
Granodiorite, Stonewall formation, Cuyamaca	1.705	1.717	1.720	0.015
Mount Hole granodiorite, Mount Hole	1.695	1.710	1.714	0.019
Tonalite, Aguanga	1.743	1.760	1.763	0.020
Sierra Nevada batholith				
Quartz monzonite, Basin Mountain	1.750	1.766	1.770	0.020
Idaho batholith				
Porphyritic granodiorite, Cascade	1.740	1.751	1.755	0.015
Granodiorite, Stanley	1.761	1.776	1.780	0.019
Granodiorite, Atlanta	1.752	1.768	1.771	0.019
White Mountains, New Hampshire				
Fresh Conway granite, Conway	1.721	1.738	1.742	0.021
Weathered Conway granite, Conway	1.720	1.737	1.740	0.020
Albany porphyritic quartz syenite, Passaconway	1.690	1.700	1.706	0.016

among its isotropic varieties. The birefringence, $\gamma - \alpha$, is shown to vary from 0.015 to 0.021 in the specimens studied. The indices of refraction of allanite from a single rock were found to be variable. The indices listed are representative. In the fresh Conway granite the allanite varies in α index from 1.695 to 1.739, and in the Cascade granodiorite the allanite varies in α index from 1.740 to 1.760.

There seems to be no clear relationship between the indices of refraction and the rock type. The Idaho minerals have consistently higher indices, whereas those from New Hampshire have lower indices. All of the allanite studied is from rocks of Late Jurassic or Cretaceous age (Larsen, 1948; Chapman, 1955; Hinds, 1934) with the exception of the New Hampshire samples which are of Mississippian age (Billings, 1945).

CHEMISTRY

Chemical analysis

Chemical analyses (Table 2) of allanite from different areas and of different optical properties were made by Glen Edgington of the Geological Survey.

TABLE 2. CHEMICAL ANALYSES, IN PER CENT, OF ALLANITE FROM CASCADE, IDAHO; CONWAY, NEW HAMPSHIRE; AND RIVERSIDE, CALIFORNIA¹

Constituent	Cascade granodiorite	Conway granite	Granite from Rubidoux Mountain, (fine), Calif.
SiO ₂	30.35	26.05	29.75
Al ₂ O ₃	7.56	7.54	8.42
Fe ₂ O ₃	18.14	17.01	20.68
CaO	12.90	10.45	8.95
MgO	1.43	0.81	0.91
MnO	0.38	0.58	0.31
H ₂ O (total)	2.00	5.60	2.40
Ce ₂ O ₃	11.06	12.45	11.38
Re ₂ O ₃ (other)	15.69	18.69	15.81
(Total RE incl. ThO ₂)	(26.75)	(31.14)	(27.19)
Total	99.51	99.18	98.61
Determined on separate samples by Sherwood ²			
ThO ₂	1.2	0.92	0.76
U	0.0036	0.0540	0.0400

¹ Analyses made by methods outlined in Hillebrand and Lundell (1929)

² Uranium determined fluorimetrically. Thoria determined colorimetrically by thoron method.

Spectroscopy

Semiquantitative spectrographic analyses of nine allanites from igneous rocks are compared in Table 3. The minerals were separated from rocks of the White Mountains batholith of New Hampshire, the Southern California batholith, the Sierra Nevada batholith, and the Idaho batholith. The rocks include fresh and weathered alkalic biotite granites, a hypersthene-bearing leucogranite, four granodiorites, a quartz monzonite and a porphyritic granodiorite. Despite variations in the optical properties, color, abundance, and origin of these allanite specimens, they are remarkably alike in composition.

Aside from the radioactive components, which are discussed separately, most of the variations in composition are within the limits of precision of the method. One immediately obvious fact is that each allanite contains the same 37 elements, with the exception of the absence of thulium from the Basin Mountain mineral and the absence of lutetium from the Cascade granodiorite mineral. The variations, which seem to be regional, are the higher content of Nb, Be, and Sn in the New Hampshire minerals, and the higher content of the elements Mn, Ti, Ni, and Cu in the Sierra Nevada specimen.

Among the rare earths, in all samples the order of abundance is Ce, (La, Nd, Pr), (Sm, Gd), variable traces of Lu, Ho, and Eu. Tm is the least abundant. Of the cerium earths the order is Ce, (La, Nd, Pr), Sm, and Eu. Of the yttrium earths the order is (Gd, Dy), (Er, Yb, Lu), (Ho, Tm.)

This distribution of rare earths shows the most pronounced cerium assemblage (Rankama and Sahama, 1950) of any of the rare-earth minerals. Goldschmidt and Thomassen (1924) describe six assemblages of rare earths occurring in minerals including an allanite-type assemblage containing the series La-Nd, minor amounts of Sm-Gd, and traces of other yttrium earths.

The sensitivity of the spectrographic method used for Na is 0.01 per cent, for K is 0.3 per cent, and for Li is 0.04 per cent. The most sensitive lines were not used for these analyses because their wavelengths are in the visible region of the spectra and the standard method covers from 2350 Å to 4750 Å.

Radioactive components

Table 4 compares the Th and U contents, calculated eU, Th/U, and optical properties of ten of the allanite samples. This radioactivity, called calculated total eU in Table 4, is calculated (for beta counting), on the assumption of the secular equilibrium of both U and Th, by taking the sum of the per cent U and one-quarter of the per cent Th. The minerals contain no detectable potassium.

TABLE 3. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF ALLANTINE
Analyst: Mona L. Franck

[illegible]

TABLE 4. RADIOACTIVE COMPONENTS OF ALLANTITE FROM IGNEOUS ROCKS

Rock and location	U ²³⁸ (per cent)	Th ²³² (per cent)	Th/U	Th as per cent eU	Calculated total eU (per cent)	Indices of refraction			γ - α
						α	β	γ	
New Hampshire Weathered Conway granite, Conway Fresh Conway granite, Conway	0.0656	2.33	35.5	0.583	0.649	1.720	1.737	1.740	0.020
	0.0540	0.92	15.1	0.202	0.256	1.721	1.738	1.742	0.021
Idaho Granodiorite, Stanley Porphyritic granodiorite, Cascade Granodiorite, Atlanta	0.0040	1.14	286.	0.286	0.296	1.761	1.776	1.780	0.019
	0.0036	1.05	291.	0.264	0.268	1.740	1.751	1.755	0.015
	0.0045	0.99	220.	0.249	0.253	1.752	1.768	1.771	0.019
California Granite from Rubidoux Mountain, fine, Riverside Granodiorite, Stonewall formation, Cuyamaca Woodson Mountain granodiorite, Temecula Woodson Mountain granodiorite, Descanso Quartz monzonite, Basin Mountain	0.0400	0.67	16.7	0.167	0.207	1.735	1.750	1.752	0.017
	0.0111	0.72	64.8	0.180	0.191	1.705	1.717	1.720	0.015
	0.0055	0.56	101.	0.141	0.146	1.735	1.750	1.753	0.018
	0.0102	0.38	37.2	0.097	0.107	1.745	1.760	1.763	0.018
	0.0078	0.35	44.6	0.088	0.096	1.750	1.766	1.770	0.020

¹ Analyst: A. M. Sherwood.

Partly because of their similarity to the rare earths in ionic radius, uranium and thorium may be incorporated in the structure of allanite. The radioactive elements accompany the rare earths in many minerals, for example, in monazite, xenotime, bastnaesite, chevkinite, doverite, and keilhauite. In the rocks studied allanite has a lesser amount of radioac-

TABLE 5. URANIUM CONTENT OF ACCESSORY ALLANITE AND OF ITS HOST ROCKS
Analysts: A. M. Sherwood, M. Molloy, and M. Schnepfe

Rock, location	U in allanite (ppm)	U in rocks (ppm)
Granites		
Biotite granite, weathered, Conway, N. H.	656	12.0
Biotite granite, fresh, Conway, N. H.	540	13.0
Leucogranite, fine, Riverside, Calif.	400	3.7
Leucogranite, coarse, Riverside, Calif.	241	4.1
Granodiorites		
California		
Mount Hole	208	5.9
Cuyamaca	111	1.5
Descanso	102	3.7
Temecula	55	1.2
Idaho		
Atlanta	45	2.3
Stanley	40	0.8
Cascade	36	1.1
Quartz monzonites		
California		
Mt. Tom quadrangle	91	7.7
Mt. Goddard quadrangle	79	5.8
Mt. Goddard quadrangle	78	3.8
Big Pine quadrangle	50	2.0
Quartz syenite		
Passaconway, N. H.	39	4.6

tive elements captured in its structure than zircon, xenotime, or monazite, and it generally approximates the radioactivity of sphene, apatite, and the rare-earth carbonates.

Table 4 shows thorium to be high in the New Hampshire and Idaho minerals and low in the California minerals, regardless of rock type. Uranium is seen to be high in the allanites from granites from both localities listed in Table 5.

Figures 1 and 2 show the relation of the calculated total per cent eU to the birefringence and to the beta index of allanite samples.

A black high-index allanite occurring in late calcite-celestite veins

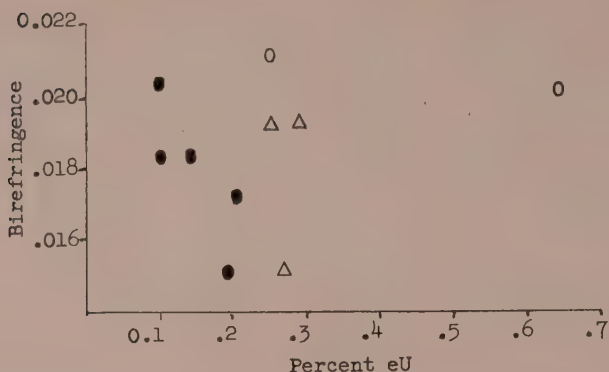


FIG. 1. Per cent eU as related to birefringence in allanite from New Hampshire \circ , Idaho \triangle , and California \bullet .

cutting rare-earth-bearing carbonate rock from Mountain Pass, California (personal communication, H. W. Jaffe, 1955) has indices of refraction of α 1.790, β 1.812, and γ 1.818; a U content of 0.0018 per cent and Th in the range of 0.01–0.1 per cent. J. P. Marble (1940) described isotropic allanite from the Baringer Hill, Texas, pegmatite with $n = 1.716$, as containing 0.715 per cent Th and 0.033 per cent U. Wells (1934) pre-

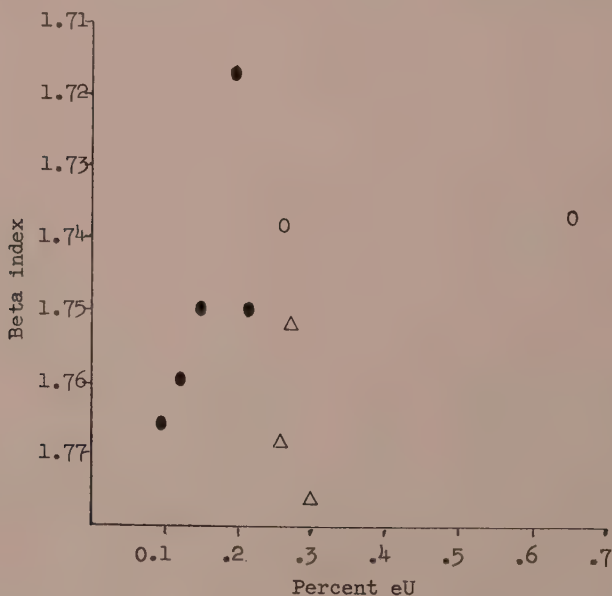


FIG. 2. Per cent eU as related to beta index in allanite from New Hampshire \circ , Idaho \triangle , and California \bullet .

sented the analysis of allanite from a Wyoming pegmatite with 1.12 per cent Th and 0.017 per cent U. Hutton (1951) describes allanite from a pegmatite in Yosemite National Park, Calif., as containing 0.95 per cent ThO₂, 0.015 per cent UO₂, and optics α 1.769, β 1.782, and γ 1.791. In a microscopic study of five specimens of black, vitreous allanite from pegmatites by E. S. Larsen, Jr., of the Geological Survey (Watson, 1917) a range from the isotropic to the birefracting forms of the mineral is

TABLE 6. URANIUM CONTENT OF EPIDOTE FROM CALIFORNIA ROCKS
Analyst: A. M. Sherwood

Rock	Uranium in epidote (ppm)
Mount Hole granodiorite	1310
Quartz monzonite, Mt. Goddard quadrangle	220
Quartz monzonite, Big Pine quadrangle	180

described. The isotropic forms show indices of refraction from $n=1.60$ to 1.72. In a study of the radioactivity of allanite from igneous rocks Hayase (1954) concluded that thorium was the major radioactive component, ranging from 0.5 to 1.6 per cent.

The uranium content of rocks varies regionally, and generally in each region the more siliceous rocks have the higher uranium content. The relationship of high uranium allanite to high uranium rocks is apparent from observation (Table 5), but it should be pointed out that only a per cent or two of the total uranium in the rocks is traceable to allanite.

For comparison three samples of epidote were analyzed and show comparatively higher uranium contents for their rock type and area (table 6). Epidote is less abundant than allanite in the rocks studied. In all the rocks epidote was green and allanite was brown or black.

PETROGRAPHY

Allanite was found to be present in the rocks studied in amounts ranging from 0.25 per cent in the granodiorite from Cascade to 0.005 per cent in the granodiorite from the Stonewall formation. The abundance of allanite in a rock has no apparent direct relation to the uranium or thorium content of the rock or mineral and is not related to rock type or area. Of 81 rocks studied, 31 were found to contain allanite. No allanite was found in any of 10 siliceous lavas from the San Juan region of Colorado. None was found in five alkalic rocks from Sussex County, New Jersey. No allanite was found in any basalts, norites, gabbros, diorites, or nepheline rocks, although geologic literature describes occasional

occurrences of allanite within such rock types (Iddings and Cross, 1885).

Table 7 lists the incidence and abundances of allanite in five suites of allanite-bearing rocks.

METAMICTIZATION

Brögger (1893) in proposing the term metamict for certain rare-earth minerals suggested, "... The reason for the amorphous rearrangement of the molecules might perhaps be sought in the lesser stability which so

TABLE 7. INCIDENCE AND ABUNDANCE OF ACCESSORY ALLANITE

Location	Number of rocks studied	Number of rocks with allanite	Percentage of allanite and rock type		
			0.X	0.0X	0.00X or less
Idaho batholith	14	6	1 granodiorite	2 granodiorites	3 granodiorites
Sierra Nevada batholith, Calif.	6	4	—	3 quartz monzonites	1 granite
Southern California batholith	34	13	1 granite	2 granodiorites 1 granite	7 granodiorites 1 quartz syenite 1 quartz monzonite
Sterling batholith, R. I.	4	3	—	1 granodiorite	2 granites
White Mountain batholith, N. H.	8	5	1 granite	2 granites 1 quartz syenite	1 granite

complicated a crystal molecule as that of these minerals must have in the presence of outside influences."* He implied that the rare-earth minerals were so complex as to prevent them from being permanently combined in the crystalline state—a definition no longer accepted.

Des Cloizeaux and Damour (1860) noted that isotropic allanite became birefringent on heating and showed that both the isotropic and birefringent allanite existed both anhydrous and hydrated.

Goldschmidt and Thomassen (1924) described the alteration of rare-earth minerals from the crystalline to the glassy state. They concluded that the important factor is the weak chemical bonding between rare earths and weak acids (silicic, tantalic). Goldschmidt proposed that for metamictization to take place the crystal lattice must have a weak enough ionic structure to permit decomposition and hydrolysis. Also, he proposed that it is necessary that radiation provide the energy to discharge the ions of the rare-earth elements. This radioactivity could be either from within or from without the crystal. Metamictization would

* Translated by A. Pabst (1952, p. 138).

thus occur as the ionic bond breaks by hydrolysis, and the lattice becomes isotropic.

Ellsworth (1925) stated that "... all minerals containing UO_2 automatically oxidize themselves at a rate depending on the rate of uranium and thorium decomposition."

Hata (1939) in describing the weathering of allanite reports the altered portions as being conspicuously high in thoria and conspicuously low in the rare earths, as compared with the fresh part of the same mineral. As the result of leaching studies, Hata concluded that the alteration is likely to take place when the ratio of Fe_2O_3 to Al_2O_3 is less than 1.3 and the content of thoria is more than 1.5 per cent. The other variables and the relative proportions of the rare earths were found to have no influence on the alteration.

Ueda and Korekawa (1954) suggest that the metamictization of allanite is due to the repeated expansion and quenching of the lattice, resulting in the formation of an aggregate of several phases in both the crystalline and amorphous state.

Allanite shows various degrees of metamictization and, in the extreme cases of some pegmatite specimens, approaches isotropism. The alteration of the allanite is suggested to be due to radiation from the uranium and thorium components which breaks the ionic bonds and permits the entry of water into the lattice of the mineral.

ACKNOWLEDGMENTS

We wish to thank Professor Esper S. Larsen, Jr., of the Geological Survey who suggested this study and who checked the optical properties of many of the allanite samples. Thanks are also due to George H. Hayfield for assistance in mineral separations, and to Glen Edgington, Marjorie Molloy, and Marian Schnepfe, also of the Geological Survey, for chemical analyses. This work is part of a program conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.

REFERENCES

- BILLINGS, M. P. (1945), Mechanics of igneous intrusion in New Hampshire: *Am. Jour. Sci.*, **243-A**, Daly Volume, 43.
- BRÖGGER, W. C. (1893), Amorf: *Salmonsens store illustrerede Konversationslexikon*: **1**, 742-743.
- CHAPMAN, R. W., GOTTFRIED, DAVID, AND WARING, C. L., (1955), Age determinations on some rocks from the Boulder batholith and other batholiths of western Montana: *Geol. Soc. America Bull.*, **66**, 607-609.
- DES CLOIZEAUX, A., AND DAMOUR, A. (1860), Examen des propriétés optiques et pyrogénétiques des minéraux connus sous les noms de gadolinites, allanites, orthites, euxenite, yrite, yttrotantalite et fergusonite: *Ann. chim. phys.* (3), **59**, 357-379.

- ELLSWORTH, H. V. (1925), Radioactive minerals as geological age indicators: *Am. Jour. Sci.*, 5th ser., **9**, 127-144.
- GOLDSCHMIDT, V. M., AND THOMASSEN, L. (1924), Geochemische Verteilungsgesetze der Elemente III: *Norske vidensk.-akad. Oslo Arbok* **5**, 51-109.
- HATA, S. (1939), The alteration of allanite: *Tokyo Inst. Phys. Chem. Res., Sci. Papers*, no. 923, **36**, 301-311.
- HAYASE, I. (1954), The radioactivity of rocks and minerals studied with nuclear emulsion. Pt. 2. Thorium content of granitic allanites: *Kyoto Imp. Univ., Coll. Sci., Mem. ser. B*, **21**, no. 2, 171-183.
- HILLEBRAND, W. F., AND LUNDELL, G. E. F. (1929), Applied inorganic analysis: New York, John Wiley & Sons.
- Hinds, N. E. A. (1934), The Jurassic age of the last granitoid intrusives in the Klamath Mountains and Sierra Nevada, California: *Am. Jour. Sci.*, 5th ser., **27**, 182-192.
- HOBBS, W. H. (1889), On the paragenesis of allanite and epidote as rock forming minerals: *Am. Jour. Sci.*, **38**, 223-228.
- HUTTON, C. O. (1951), Allanite from Yosemite National Park, Tuolumne Co., Calif.: *Am. Mineral.*, **36**, 233-248.
- IDDINGS, J. P., AND CROSS, W. (1885), On the widespread occurrence of allanite as an accessory constituent of many rocks: *Am. Jour. Sci.*, 3d ser., **30**, 108-111.
- MARBLE, J. P. (1940), Allanite from Barringer Hill, Texas: *Am. Mineral.*, **25**, p. 168-173.
- PABST, A. (1952), The metamict state: *Am. Mineral.*, **37**, 137-157.
- RANKAMA, K., AND SAHAMA, TH. G. (1950), Geochemistry, Univ. Chicago Press.
- UEDA, T., AND KOREKAWA, M. (1954), On the metamictization: *Kyoto Imp. Univ., Coll. Sci., Mem.*, ser. B, **21**, no. 2, 151-162.
- WATSON, T. L. (1917), Weathering of allanite: *Geol. Soc. America Bull.*, **28**, 463-500.
- WELLS, R. C. (1934), Allanite from Wyoming: *Am. Mineral.*, **19**, 81-82.

Manuscript received November 11, 1956

LARNITE, SCAWTITE, AND HYDROGROSSULAR FROM TOKATOKA, NEW ZEALAND

BRIAN MASON, *The American Museum of Natural History,*
New York 24, N.Y.

ABSTRACT

Near Tokatoka, North Auckland, New Zealand an andesite dike, probably of Pliocene age, has metamorphosed the surrounding limestone of the Onerahi Formation (Lower Tertiary). A marked mineralogical zoning parallel to the contact is noteworthy; from the contact outwards these zones consist largely of (1) hydrogrossular, thickness 6 inches; (2) larnite, thickness 30 inches; (3) scawtite, thickness 10 inches. Other minerals recognized include cristobalite, opal, spurrite, gehlenite, and wollastonite. The minerals are described in detail, and the maximum temperature during metamorphism is estimated to be about 800°.

INTRODUCTION

Near Tokatoka, North Auckland, New Zealand (approx. latitude 36° S, longitude 174° E) numerous small bodies of intermediate and basic igneous rocks intrude the country rock, which is mainly argillaceous limestone of the Onerahi Formation (Lower Tertiary). The regional geology has been mapped by the New Zealand Geological Survey (Ferrar, 1934). While searching the country rock for fossils my brother, Mr. A. P. Mason, observed an andesite dike well exposed in a small quarry opened for road material and drew my attention to it. It proved to have produced a well-defined zone of contact metamorphism in the enclosing limestone. Natural exposures are poor in this region, and it was a fortunate chance that this quarry was observed shortly after it had been opened.

The exact location according to the National Grid is N27/533560, and it is 2.1 miles due east of the Tokatoka Hotel. The andesite dike forms the backbone of a narrow ridge. When visited in December 1953 the quarry was about 20 feet deep and had been opened for about 50 feet along the strike (N. 20° E., dip 60° SE) of the dike.

The dike is about 12 feet thick, and consists throughout of a fine-grained grey andesite. No attempt was made to trace its extension beyond the quarry, but according to Ferrar's map it can be followed for about 400 yards before it is obscured by Recent swamp deposits. The zone of contact metamorphism in the enclosing limestone is clearly marked by the presence of a band of dense black rock which does not effervesce with acid—the larnite zone.

Detailed collection from the contact zone on the east side of the quarry showed that the contact with the andesite is a sharp one (Fig. 1). At the

contact itself the limestone has been changed to a white rock consisting largely of hydrogrossular. This rock continues for about six inches from the contact, when it passes rapidly into dense black larnite rock. This zone is about thirty inches wide, and is followed by a greyish-white band, about ten inches wide, of rock consisting mainly of scawtite. Beyond this scawtite zone is pale grey limestone, seamed with narrow (1 mm. and



FIG. 1. Close-up of contact between andesite and limestone; the hammer head rests on the knife-sharp contact.

less) white veinlets of grossularite and wollastonite. On the western side of the quarry a similar sequence was found, except that the scawtite zone was not observed; it may be present but has been overlooked.

MINERALOGY AND PETROLOGY

Andesite: In hand specimen the andesite is an aphanitic grey rock; it was mapped as basalt by Ferrar, evidently on megascopic appearance. In thin section it is seen to consist largely of oligoclase laths (average dimensions 0.1×0.02 mm.) with a marked trachytic texture. The only other minerals present are rare plagioclase (An_{60}) phenocrysts, minute (0.01 mm. diameter) crystals of magnetite, and interstitial pale green ferromagnesian silicate, specifically indeterminable but probably chlorite. The density of the rock is 2.62. The andesite shows no chilled margin against the country rock and the grain size of the feldspar is not noticeably smaller towards the contact.

The chemical composition and norm (calculated according to Barth, 1952, p. 80) are given in Table 1. This confirms the classification of the rock as an andesite, with trachytic affinities as indicated by the presence of 14% orthoclase in the norm. Orthoclase was not recognized in thin sections, although if present it could easily be overlooked. In chemical and mineralogical composition and in mode of occurrence this rock resembles kullaite, from Kullen near Kristianstad in southern Sweden.

TABLE 1. ANALYSIS AND NORM OF ANDESITE, ONE INCH FROM CONTACT WITH LIMESTONE

(Analyst: Doris Thaemlitz, Rock Analysis Laboratory, University of Minnesota; Lab. No. R2213)

	Weight, per cent	Mol. Prop.	Norm	
SiO ₂	51.90	8607	Or	14.5
TiO ₂	0.82	102	Ab	43.5
Al ₂ O ₃	17.01	1664	An	17.3
Fe ₂ O ₃	2.95	185	Cn	2.5
FeO	5.00	696	Σ salic	77.8
MnO	0.17	24		
MgO	3.67	910	Di	6.8
CaO	5.26	938	Hy	5.0
BaO	1.26	82	Ol	5.4
Na ₂ O	4.58	739	Mt	3.3
K ₂ O	2.34	248	Il	1.2
P ₂ O ₅	0.28	20	Ap	0.5
CO ₂	0.15			
H ₂ O+	3.34		Σ femic	22.2
H ₂ O-	1.25			
S	0.06			
	100.04			

A noteworthy feature of the chemical analysis is the unusually high content of barium, which is presumably present in the feldspar, since no specific barium minerals were noted in thin sections. Von Engelhardt (1936), who studied the geochemistry of barium, recorded that rocks of the syenite-trachyte family show the largest concentration, averaging about 0.2% BaO. The presence of 1.26% BaO in the Tokatoka andesite is intriguing, since other igneous rocks from this region do not show unusual amounts of barium; it can hardly have been derived by assimilation, since barium was not detected in the limestone, and in any case there is no evidence of assimilation having taken place.

Limestone: The limestone is a pale grey fine-grained rock, compact but well jointed, and it breaks down rapidly by weathering. It is very uniform in texture and shows no trace of fossils. It belongs to the Onerahi Formation, which covers large areas in North Auckland, but whose age is not precisely known; various ages, from Upper Cretaceous to Oligocene, have been ascribed to it, and it may extend through a considerable time interval.

TABLE 2. ANALYSES OF LIMESTONE, (1) UNALTERED, AND (2) SLIGHTLY ALTERED

(1) Onerahi limestone, near Kaiwaka, North Auckland (*N.Z. Geol. Surv. Bull.* 22, 61).

(2) Onerahi limestone, eight feet from contact with andesite dike.

(Analyst: Doris Thaemlitz, Rock Analysis Laboratory, University of Minnesota; Lab. No. R2214).

	(1)	(2)	Mol. Prop.	Grossu- larite	Scaw- tite	Wollas- tonite	Calcite
SiO ₂	17.48	19.51	3248	927	1101	1220	
Al ₂ O ₃	3.01	2.59	254	309			
Fe ₂ O ₃	1.61	0.88	55				
FeO	—	0.20	28				
MgO	0.78	0.56	139	927	1285	1220	5496
CaO	41.49	50.04	8923				
CO ₂	32.00	25.00	5680		184		5496
H ₂ O+	3.03	0.66	367		367		
H ₂ O—	—	0.12					
P ₂ O ₅	—	0.10					
TiO ₂	—	0.14					
MnO	—	0.05					
	99.40	99.85					

In thin section the limestone is seen to be a structureless aggregate of irregular grains of calcite, averaging about 0.03 mm. in diameter. The fine grain and the complete absence of any trace of fossils suggest that the limestone was formed by inorganic precipitation.

A sample of the limestone eight feet from the contact with the dike was selected for analysis (Table 2). This limestone appeared to be completely unaltered except for some microscopic veinlets of garnet; the residue from dissolving the rock in dilute acid gave an x-ray powder pattern of grossularite with $a=11.90\text{\AA}$. A cursory examination of the analysis, however, shows that it cannot be interpreted as a mixture of calcite and grossularite; there is an excess of CaO and a deficiency of CO₂. A careful examination of thin sections of this rock showed that associated

with the grossularite are patches of a fibrous or prismatic mineral with low birefringence; wollastonite was suspected, and was confirmed by the recognition of the strongest lines of wollastonite in an *x*-ray powder photograph of the analysed material. Reexamination of the thin sections also showed the presence of some scawtite, which is similar in appearance to calcite, but has brighter interference colors. The mode calculated from the analysis is calcite 55%, grossularite 14%, wollastonite 14%, and scawtite 15%; the deficiency from 100% is due to a slight excess of CaO, and the other oxides present which are not used in the calculated mode.

In view of the somewhat metamorphosed state of the analysed sample, an analysis of typical unmetamorphosed Onerahi limestone has been selected from the literature and is also given in Table 2. It can be seen that the beginning alteration is essentially a decarbonation, the silica and alumina necessary for the formation of grossularite, wollastonite, and scawtite being provided by the impurities in the limestone.

Hydrogrossular zone: The innermost contact zone against the dike is four to six inches thick, and consists of white massive material, often chalky in appearance and very light and porous. Thin sections of this material showed tiny (0.01 mm. diameter) rounded isotropic grains with high refractive index in a turbid, isotropic or slightly anisotropic groundmass of low refractive index. *X*-ray powder photographs served to identify the rounded grains as hydrogrossular, and the groundmass as cristobalite (the high-temperature or beta-form) probably admixed with opal. The cristobalite was identified by the strong lines with *d*-values 4.15, 2.53, and 1.64; the presence of opal is suggested by a diffuse halo in the powder photographs at *d*=4.0.

The *x*-ray powder photograph of hydrogrossular is similar to that of grossularite, but the lines are weaker and back reflections seldom appear even after long exposure. The cell dimensions vary considerably from specimen to specimen, the range being from 11.95 Å to 12.24 Å; considering hydrogrossular as a phase in the two-component system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ — $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$, this indicates a compositional range from 25% to 65% of the $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ component, according to Yoder's data (1950, fig. 14). The composition bears no obvious relation to the location of the material with respect to the contact; different samples from the hydrogrossular zone have cell dimensions ranging from 11.95 Å to 12.24 Å, and hydrogrossular with *a*=12.17 Å occurs as disseminated grains in the scawtite zone. The garnet in veinlets in the limestone, beyond the scawtite zone, has *a*=11.90 Å and is evidently close to grossularite in composition; the slightly greater cell dimensions than pure grossularite (*a*=11.85 Å) are probably due to a small amount of ferric iron replacing aluminum, rather than the presence of hydroxyl.

Four names are current for minerals with composition between $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ —hibschite (Cornu, 1905), plazolite (Foshag, 1920), grossularoid (Belyankin and Petrov, 1941), and hydrogrossular (Hutton, 1943). Later work, especially that of Yoder (1950), has shown that a continuous series exists between the above components, and that the individual species that have been described are simply random compositions within this series. Under these circumstances a single name is adequate. In this paper hydrogrossular is accepted as the most satisfactory name, although hibschite has priority. The name hydrogrossular indicates clearly the nature of the mineral. The variation in cell dimensions for samples taken from a single small hand specimen shows that the composition of hydrogrossular can vary greatly over a short distance. Thus specific formulas such as have been derived for plazolite and hibschite misrepresent the true composition; a satisfactory formula is that suggested by Hutton— $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-m}(\text{OH})_{4m}$. Although Hutton introduced the name hydrogrossular for compositions intermediate between grossularite and hibschite (and plazolite), it seems reasonable to extend the name to include the latter minerals also.

A sample of the material from the inner contact zone was analysed chemically (Table 3). The hydrogrossular in this sample had the largest cell dimensions, $a = 12.24 \text{ \AA}$, indicating a composition approximately $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$, according to Yoder's data. When the chemical analysis is interpreted in these terms, it indicates a composition approximately 59% cristobalite and opal, 40% hydrogrossular, and 1% calcite. The SO_3 and P_2O_5 shown by the analysis may well be present as SO_4 groups and PO_4 groups in the hydrogrossular, since the garnet structure is known to tolerate the introduction of other four-coordinate cations in place of silicon.

On cursory consideration the presence of silica in the form of cristobalite rather than quartz appears anomalous, since the temperature of formation of the material was certainly far outside the stability field of cristobalite in the system SiO_2 . However, the material was probably formed rapidly under non-equilibrium conditions, through the agency of hot magmatic gases; also the cristobalite may be stabilized by the presence of foreign ions buttressing the open structure of this mineral and preventing its inversion to quartz.

Larnite zone: The larnite zone is very prominent, forming a band about thirty inches thick, dark grey to almost black in color, hard, flinty, and very tough. The dark color is not due to the larnite, but to the presence of a small amount of very fine-grained magnetite. Pure larnite is presumably white. It is interesting to note that the original larnite from Larne is grey from the presence of finely divided spinel.

Thin sections of this rock show the larnite as an aggregate of tiny rounded grains, seldom greater than 0.02 mm. in diameter. On this account the optical properties are not easily determined, and in immersion liquids only the maximum and minimum refractive indices were measured: $\alpha = 1.71$, $\gamma = 1.73$. The identification was originally made on

TABLE 3. ANALYSIS OF HYDROGROSSULAR-CRISTOBALITE ROCK, FROM
CONTACT WITH ANDESITE DIKE

(Analyst: Eileen H. Oslund, Rock Analysis Laboratory, University of Minnesota;
Lab. No. R2215)

	Weight per cent	Mol. Prop.	Calcite	Hydrogros- sular	Cristobalite Opal
SiO ₂	59.03	9789		924	8865
Al ₂ O ₃	8.15	797		924	
Fe ₂ O ₃	2.03	127			
FeO	0.19	26			
MgO	3.25	806		2772	
CaO	13.63	2430	139		
CO ₂	0.61	139	139		
H ₂ O+	7.02	3900		3696	204
H ₂ O-	4.48	2489			2489
TiO ₂	0.29				
MnO	0.09				
BaO	0.10				
Na ₂ O	0.13				
K ₂ O	0.08				
SO ₃	0.59				
P ₂ O ₅	0.22				
	99.89				

the x-ray powder photograph, which agreed with that given by Brown-miller and Bogue (1930) for synthetic beta dicalcium silicate. This has been confirmed by Dr. Della M. Roy of the Pennsylvania State University, who very kindly ran the Tokatoka larnite on an x-ray diffractometer and compared the record with that for a sample of beta dicalcium silicate prepared in her laboratory. She also detected a small amount of gehlenite intermixed with the larnite.

The larnite rock also contains some spurrite, which occurs as porphyroblasts up to about 0.15 mm. in diameter; a little scawtite in isolated patches; and a small amount of finely divided magnetite. The density of the rock varies somewhat from sample to sample on account of variable mineral composition; the maximum density measured, probably for material nearly pure larnite, was 3.26.

A sample of the larnite rock was analysed chemically, and the results are given in Table 4. Assuming ideal compositions corresponding to the accepted chemical formulas of the minerals, the calculated mode is 59% larnite, 21% spurrite, 11% gehlenite, 5% scawtite, and 1% magnetite, the deficiency from 100% being due to excess H_2O+ and other oxides not used in the calculation.

TABLE 4. ANALYSIS OF LARNITE ROCK, EIGHT INCHES FROM
MARGIN OF ANDESITE DIKE

(Analyst: Eileen H. Oslund, Rock Analysis Laboratory, University of Minnesota;
Lab. No. R2216)

	Weight per cent	Mol. Prop.	Magne- tite	Gehlen- ite	Scaw- tite	Spur- rite	Larnite
SiO ₂	30.89	5123		408	383	958	3374
Al ₂ O ₃	4.17	408		408			
Fe ₂ O ₃	0.89	56	56				
FeO	0.54	75	56				
MgO	0.72	179		} 816	447	2395	6748
CaO	57.26	10208					
CO ₂	2.39	543			64	479	
H ₂ O+	1.60	888			128		
H ₂ O—	0.66						
Na ₂ O	0.17						
K ₂ O	0.09						
TiO ₂	0.21						
P ₂ O ₅	0.14						
MnO	0.06						
BaO	0.00						
SO ₃	0.38						
	100.17						

The beta form of dicalcium silicate is rather difficult to preserve in synthetic preparations, since it undergoes an inversion below 675° to the gamma form. The gamma form has the olivine structure and is considerably less dense than the beta form. The increase of volume on inversion causes solid masses of the beta form to fall to powder. This feature was observed on the original larnite when it was heated or hammered (Tilley, 1929, p. 82). The larnite from Tokatoka does not invert to gamma dicalcium silicate on heating or hammering. This reluctance to invert is probably the result of the presence of foreign ions in solid solution inhibiting the change, a feature characteristic of the beta dicalcium silicate from slags (Mason, 1945, p. 179).

This appears to be the third record of beta dicalcium silicate as a mineral, and the first outside Great Britain. Besides the original discovery at Scawt Hill, it has been found in a dolerite-chalk contact at Ballycraigy, also in the Larne district (McConnell, 1955), and on the island of Muck in Scotland (Tilley, 1947).

Scawtite zone: A zone about ten inches thick between the larnite zone and the limestone consists essentially of scawtite. The scawtite rock is greyish-white, dense and flinty and with a marked conchoidal fracture. It effervesces in cold dilute hydrochloric acid, but less actively than the limestone. Thin sections show that the rock is an aggregate of very small grains of scawtite, the individual diameters being seldom greater than 0.01 mm. On this account the optical properties are not easily determined, and only the maximum and minimum refractive indices were measured: $\alpha = 1.60$, $\gamma = 1.62$. The mineral was identified from its *x*-ray powder photograph, which agrees with that given for scawtite from Ballycraigy by McConnell (1955). The scawtite rock also contains some hydrogrossular as small disseminated grains, a little magnetite, and occasional patches of calcite, which can be distinguished from the scawtite by its higher birefringence.

A chemical analysis of the scawtite rock is given in Table 5. The calculated mode (using a composition halfway between $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ for the hydrogrossular, as indicated by its cell dimensions, $a = 12.17\text{\AA}$) is 66% scawtite, 17% hydrogrossular, 12% calcite, and 2% magnetite. When the analysis is recalculated in this way a small amount of CaO and $\text{H}_2\text{O}+$ remains unaccounted for. In addition there is the 0.70% SO_3 , which has not been identified with a specific mineral; it may conceivably be present as sulphate groups in the structure of the hydrogrossular.

This is the fifth record of scawtite, the other localities being Scawt Hill (Tilley, 1930) and Ballycraigy (McConnell, 1955) in Northern Ireland; near Neihart, Montana (Taylor, 1935); and Crestmore, California (Murdoch, 1955).

PARAGENESIS

The source of the heat which produced the metamorphism is clearly the magma from which the andesite crystallized. The temperature at which magma of this composition flows freely (and the narrowness of the dike indicates that the magma did flow freely) is uncertain. Zies (1941) has recorded that the temperature of the andesitic lava of the extruding dome at the volcano of Santiaguito in Guatemala was about 700° ; this was the temperature at the top of the dome, and the tempera-

tures within the magma channel were undoubtedly higher. Probably the temperature of the magma at Tokatoka was at least 800°–900°.

The pressure due to the overlying rock was certainly quite low, since there is no evidence for any great thickness having been removed by erosion since the igneous activity. Many of the small igneous intrusions in this region of North Auckland reached the surface and gave rise to lava flows.

TABLE 5. ANALYSIS OF SCAWTITE ROCK, 3½ FEET FROM THE MARGIN OF THE ANDESITE DIKE

Analyst: Doris Thaemlitz, Rock Analysis Laboratory, University of Minnesota; Lab. No. R22127)

	Weight per cent	Mol. Prop.	Magnetite	Hydro- grossular	Scawtite	Calcite
SiO ₂	32.22	5343		606	4737	
Al ₂ O ₃	4.13	404		404		
Fe ₂ O ₃	1.23	77	77			
FeO	0.33	46	46			
MgO	0.80	198	31			
CaO	45.34	8083		} 1212	5530	1182
CO ₂	8.68	1972			790	1182
H ₂ O+	5.77	3203		1212	1580	
H ₂ O+	0.14					
Na ₂ O	0.01					
K ₂ O	0.04					
TiO ₂	0.23					
P ₂ O ₅	0.15					
MnO	0.07					
BaO	0.20					
SO ₃	0.70					
	100.04					

It is thus reasonable to conclude that during the active flow of magma through the dike conduit the temperature at the margin was above 800°, and the rock pressure was comparatively low. According to Yoder (1950) the association larnite-gehlenite in a metamorphosed limestone indicates a temperature of formation of 800°; at lower temperature the association would be larnite-grossularite for compositions low in Al₂O₃, or grossularite-gehlenite for compositions higher in Al₂O₃.

From these two lines of evidence it therefore seems probable that the maximum temperature in the larnite zone, which extends as far as two feet from the margin of the dike, was at least 800°. However, the larnite

zone does not extend to the dike itself; along the margin of the dike there is a band of hydrogrossular-cristobalite rock up to six inches thick. Yoder's studies show that hydrogrossular of this composition is formed at about 500°.

We thus have the apparent contradiction of a lower temperature zone at the margin of the dike, followed by a higher temperature zone further out. This contradiction is resolved, however, if the hydrogrossular-cristobalite zone is the result of late metasomatism of the inner part of the larnite zone. Their relative compositions suggests such a relationship; the hydrogrossular-cristobalite rock is highly hydrated and silicated with reference to the other metamorphic zones, and it is reasonable to ascribe this to the introduction of SiO_2 and H_2O during the ultimate cooling and crystallization of the andesite. On this hypothesis the larnite zone originally extended to the margin of the dike, and the innermost part was converted to hydrogrossular and cristobalite by later introduction of silica, water, and some alumina.

The presence of scawtite as a rock-forming mineral constituting a distinct metamorphic zone seems to be unique among the few occurrences of this mineral. At other localities scawtite is found lining veins or vesicles in contact-altered limestones, and evidently is of late hydrothermal origin. At Tokatoka it is the principal mineral in a zone about ten inches thick between the larnite zone and the limestone, and also occurs in sporadic patches further out in the apparently unaltered limestone.

It might be suggested that the scawtite is not a primary metamorphic product but is secondary after some pre-existing mineral (as hydrogrossular in the inner contact zone is evidently secondary after larnite and gehlenite). The differences in composition between the larnite rock and the scawtite rock are not great, being essentially an increase of CO_2 and H_2O and decrease of CaO in the latter. These differences can be interpreted as the result either of metasomatism of the larnite rock, or of a lower temperature of metamorphism, within which scawtite formed as a stable phase in a chemical environment essentially the same as that which gave rise to the larnite-gehlenite association closer to the intrusion. The latter interpretation is favored, mainly because of the apparently primary nature of the scawtite; thin sections indicate that it originated by the direct replacement of the limestone, rather than by metasomatism of the larnite rock.

Another possibility is that scawtite is secondary after wollastonite. The formula of scawtite ($6\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$) shows that in composition it is essentially a somewhat carbonated and hydrated wollastonite, and its structure is probably related to that mineral (McConnell, 1955). Hydration of a wollastonite-calcite rock could conceivably give

rise to scawtite. This is a plausible hypothesis, since the original presence of a wollastonite zone might be expected. However, no trace of residual wollastonite was seen in the scawtite rock, and the evidence favors a primary origin for the scawtite.

An interesting feature which deserves comment is the variation in composition of the garnet in the contact zone. The material in the inner contact zone is hydrogrossular of variable composition, and hydrogrossular also occurs disseminated through the scawtite zone, but the garnet in the tiny veinlets in otherwise unaltered limestone is close to grossularite in composition and is evidently not hydrated. Thus the garnet does not increase regularly in hydration from the contact outwards, which would be expected were it produced along a line of steadily diminishing temperature. The reason for the hydrated nature of the garnet in the inner contact zone has already been discussed in the description of hydrogrossular. The anhydrous nature of the grossularite in the limestone suggests that it formed at comparatively high temperatures. A reasonable explanation is that it was produced by the action of hot gases escaping from the magma, an explanation supported by the occurrence of the mineral along narrow veinlets, which were probably microscopic joints in the limestone serving to channel the gases from the intrusion. The presence of wollastonite with the grossularite in the veinlets indicates that they were formed at temperatures above 500°, from the data of Harker and Tuttle (1956) on the calcite-wollastonite reaction.

Tilley (1950) has recently discussed the progressive metamorphism of siliceous limestones (Fig. 2). He recognizes successive steps of progressive decarbonation giving rise to the following mineral associations: (1) wollastonite-calcite; (2) wollastonite-tilleyite-calcite; (3) wollastonite-spurrite-calcite; (4) spurrite-rankinite; (5) spurrite-larnite. The succession at Tokatoka is not as complete as this scheme; rankinite and tilleyite have not been found, and wollastonite occurs only in small amount with grossularite in veinlets in the limestone. The association wollastonite-calcite is represented at Tokatoka by the association scawtite-calcite. Thus we have the larnite-spurrite zone followed by a scawtite-calcite zone; between them there may well be a transitional zone of spurrite-scawtite, equivalent to the wollastonite-spurrite-calcite association of Tilley's scheme. The occurrence of scawtite instead of the usual association wollastonite-calcite is the most interesting feature of the Tokatoka paragenesis. Evidently some peculiarity either in physical conditions or chemical composition or both favored the formation of scawtite, and it appeared in the sequence of metamorphism where

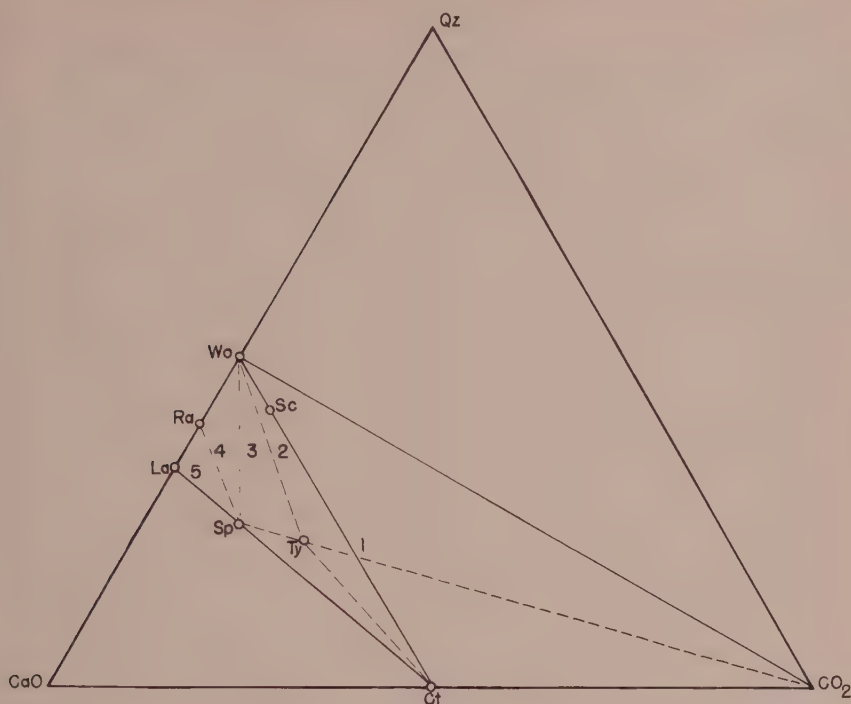


FIG. 2. Progressive decarbonation in the system $\text{CaO-SiO}_2\text{-CO}_2$ in thermal metamorphism (after Tilley, 1951); Qz=quartz, Ct=calcite, Wo=wollastonite, Ty=tilleyite, Sp=spurrite, Ra=rankinite, La=larnite, Sc=scawtite.

wollastonite would normally be expected. Perhaps an unusually high H_2O pressure, either emanating from the intrusion or resulting from a high water content in the limestone, favored the hydrated mineral scawtite over the anhydrous wollastonite.

ACKNOWLEDGMENTS

In addition to the persons mentioned in the text, I am indebted to Mr. Leineweber, of the Johns Manville Research Center, for making a preliminary spectrographic analysis and an x -ray diffractometer record of the hydrogrossular-cristobalite rock; and to Dr. R. N. Brothers, of Auckland University College, for the photograph of the quarry. My thanks are also due to the John Simon Guggenheim Memorial Foundation, as the field work was carried out during the tenure of a fellowship from this organization.

REFERENCES

- BARTH, T. F. W. (1952), Theoretical petrology. John Wiley and Sons, New York.
- BELYANKIN, D. S., AND PETROV, V. P. (1941), The grossularoid group: *Am. Mineral.*, **26**, 450-453.
- BROWNMILLER, L. F., AND BOGUE, R. H. (1930), The *x*-ray method applied to a study of the constitution of Portland cement: *Am. Jour. Sci.*, **20**, 241-264.
- CORNU, F. (1906), Beiträge zur Petrographie des Böhmisches Mittelgebirges: *Tschermaks Min. Petr. Mitt.*, **25**, 249-268.
- ENGELHARDT, W. VON (1936), Die Geochemie des Barium: *Chemie der Erde*, **10**, 189-246.
- FERRAR, H. T. (1934), The geology of the Dargaville-Rodney subdivision: *New Zealand Geol. Surv. Bull.*, **34**, 86 pp.
- FOSHAG, W. F. (1920), Plazolite, a new mineral: *Am. Mineral.*, **5**, 183-185.
- HARKER, R. I., AND TUTTLE, O. F. (1956), Experimental data on the P-T curve for the reaction: calcite + quartz \rightleftharpoons wollastonite + carbon dioxide: *Am. Jour. Sci.*, **254**, 239-256.
- HUTTON, C. O. (1943), Hydrogrossular, a new mineral of the garnet-hydrogarnet series: *Trans. Royal Soc. New Zealand*, **73**, 174-180.
- MASON, B. (1945), Basiska martinslaggers mineralogiska byggnad: *Jernkontorets Annaler*, **129**, 171-1847.
- MCCONNELL, J. D. C. (1955), A chemical, optical and *x*-ray study of scawtite from Ballycraigy, Larne, North Ireland: *Am. Mineral.*, **40**, 510-514.
- MURDOCH, J. (1955), Scawtite from Crestmore, California: *Am. Mineral.*, **40**, 505-509.
- TAYLOR, J. H. (1935), A contact metamorphic zone from the Little Belt Mountains, Montana: *Am. Mineral.*, **20**, 120-128.
- TILLEY, C. E. (1929), On larnite (calcium orthosilicate, a new mineral) and its associated minerals from the limestone contact-zone of Scawt Hill, Co. Antrim: *Mineral. Mag.*, **22**, 77-86.
- (1930), Scawtite, a new mineral from Scawt Hill, Co. Antrim: *Mineral. Mag.*, **22**, 222-224.
- (1947), The gabbro-limestone contact of Camas Mor, Muck, Inverness-shire: *Bull. Comm. Geol. Finlande*, **140**, 97-106.
- (1951), A note on the progressive metamorphism of siliceous limestones and dolomites: *Geol. Mag.*, **88**, 175-178.
- YODER, H. S. (1950), Stability relations of grossularite: *Jour. Geol.*, **58**, 221-253.
- ZIES, E. G. (1941), Temperatures of volcanoes, fumaroles, and hot springs, in "Temperature, its measurement and control in science and industry." Reinhold Publishing Corp., New York.

Manuscript received November 16, 1956.

A TECHNIQUE FOR THE ISOLATION OF MONTMORILLONITE AND HALLOYSITE

F. C. LOUGHNAN, *The New South Wales University of Technology, Kensington, New South Wales.*

ABSTRACT

A technique is presented for the complete separation of montmorillonite and/or halloysite from other minerals occurring in artificial admixtures and natural clays. The technique is based on differences in specific gravity assumed by these minerals in a solution of alcohol and bromoform.

Techniques at present being employed for the quantitative determination of the clay minerals present in natural clays may be grouped under (a) those based on the characteristics of differential thermal graphs (1,2) (b) those based on the intensity of x-ray peaks (3) and (c) those based on chemical analysis in conjunction with other properties such as cation exchange (4). It is doubtful if any of these techniques afford results better than plus or minus five per cent, though some workers have claimed greater accuracy.

Methods so far used for the isolation of the clay minerals are less effective. The one most commonly employed, based on the preferred particle size for the minerals, generally permits a concentration, but rarely yields a complete separation for the required mineral, and moreover, fails to give a full particle size range for the mineral being isolated. More recently Buzagh and Szepesi (5) have presented a technique for the isolation of montmorillonites from mixed clay samples based on the stability of the sodium clay in an alcohol-water suspending medium.

In the present paper, the complete separation of montmorillonite and halloysite is demonstrated, utilizing the apparent specific gravity assumed by these minerals when suspended in a solution of ethyl alcohol and bromoform. The extension of the technique to include illite, kaolinite and quartz generally permits the concentration of these minerals, but, since particle size is an important factor, the results are less satisfactory.

EXPERIMENTAL TECHNIQUES

Determination of the Apparent Specific Gravity of Reference Minerals.

Two relatively pure samples of each of kaolinite, halloysite and montmorillonite and one of illite were used as reference minerals. A crystal of quartz was crushed to varying sieve sizes and subjected to the same procedure as that of the other minerals. The apparent specific gravities assumed by these minerals in a solution of alcohol and bromo-

form was determined by the following procedure. Samples of 500 mg. of each mineral, previously ground to minus 200 mesh, were placed in a centrifuge tube containing bromoform. The bromoform was then diluted with alcohol, thoroughly shaken for ten minutes on a flask shaker, allowed to stand a further ten minutes, then centrifuged. The process of

TABLE 1. REFERENCE MINERALS

Mineral	Location	Apparent S.G.
S.1 Kaolinite	St. Ives, N.S.W.	2.34
S.2 Kaolinite	Huber	2.37
S.3 Halloysite	Eureka, Utah	2.17
S.4 Halloysite	Bedford, Indiana	2.19
S.5 Illite	Fithian, Illinois	2.27
S.6 Montmorillonite	Wingen, N.S.W.	1.85
S.7 Montmorillonite	Algeria	1.85
Quartz	Minus 270 Mesh	2.35
Quartz	200-270 Mesh	2.45

alcohol dilution was continued until the mineral just remained suspended. (Actually it was found that there was a range for the critical specific gravities and the values quoted below represent means.) The solution was filtered and the specific gravity determined by a micro-Westphal balance. Table 1 gives the localities of the reference minerals and their apparent specific gravities, and Table 2 the chemical analyses. Fig. 1 shows the differential thermal analysis curves for these reference minerals, as well as additional natural clays discussed later.

TABLE 2. CHEMICAL ANALYSES OF REFERENCE MINERALS

	S1	S2	S3	S4	S5	S6	S7
SiO ₂	43.1	45.1	43.6	44.3	51.1	51.6	59.7
Al ₂ O ₃	34.0	37.7	40.3	39.1	26.1	16.9	18.6
Fe ₂ O ₃	0.67	0.7	0.4	0.4	6.1	5.6	1.7
TiO ₂	5.73	1.4	0.1	0.1	0.6	0.4	0.03
CaO	—	—	—	—	—	3.63	1.11
MgO	—	—	—	—	—	1.33	—
K ₂ O	—	—	—	—	6.1	0.54	0.34
H ₂ O	12.30	13.9	14.7	13.4	7.3	11.82	6.09
H ₂ O—	3.00	0.9	2.5	4.0	—	8.59	9.12
Total	98.80	99.7	101.6	97.3	100.4	100.4	96.7

Separation of An Artificial Mixture of Clay Minerals

A sample of 100 mg. of each S1, S3, S5 and S6, together with a similar amount of quartz crushed to pass 150 mesh but retained on a 200 mesh sieve, was placed in a centrifuge tube of 23 mm. diameter containing a bromoform-alcohol solution with a specific gravity of 2.05. The tube and

TABLE 3. CHEMICAL ANALYSES OF NATURAL CLAYS

	I	II	III
SiO ₂	50.9	63.3	48.7
Al ₂ O ₃	24.4	16.7	15.6
Fe ₂ O ₃	3.61	4.75	7.48
TiO ₂	1.68	1.13	0.33
CaO	0.19	0.81	—
MgO	1.44	0.33	—
K ₂ O	0.84	2.28	1.12
H ₂ O	9.01	3.07	5.35
H ₂ O—	7.62	5.50	16.85
Total	99.7	97.9	95.4

I—Fullers earth from Dubbo, N.S.W.

II—Shale underlying the bentonite deposit at Wingen, N.S.W.

III—Montmorillonite from the alteration of andesitic basalt, Barraba, N.S.W.

contents were shaken for ten minutes on a flask shaker, permitted to stand a further ten minutes and then centrifuged. The tube was stoppered throughout the whole procedure. The supernatant liquid containing the light fraction was decanted, and the clay removed, dried and *x*-rayed. It was found to be pure montmorillonite.

The above procedure was repeated on the remaining heavy fraction, using successively solutions with specific gravities of 2.20, 2.30 and 2.40; the light fractions representing halloysite, illite and kaolinite respectively. The halloysite fraction was found to be pure when *x*-rayed, but the illite, kaolinite and remaining quartz fraction showed mutual con-

TABLE 4. COMPOSITION OF NATURAL CLAYS

Sample No.	Montmorillonite	Halloysite	Remainder
I	6%	76%	Predominantly quartz with a little kaolinite
II	31%	—	Quartz with approx. 20% kaolinite
III	87%	—	Predominantly feldspar

tamination. In all cases, however, a concentration exceeding 80% was obtained.

Separation of Montmorillonite and Halloysite from Natural Clays

A modification of the above procedure was then applied to three natural clays. They were first dispersed in water using calgon as a dis-

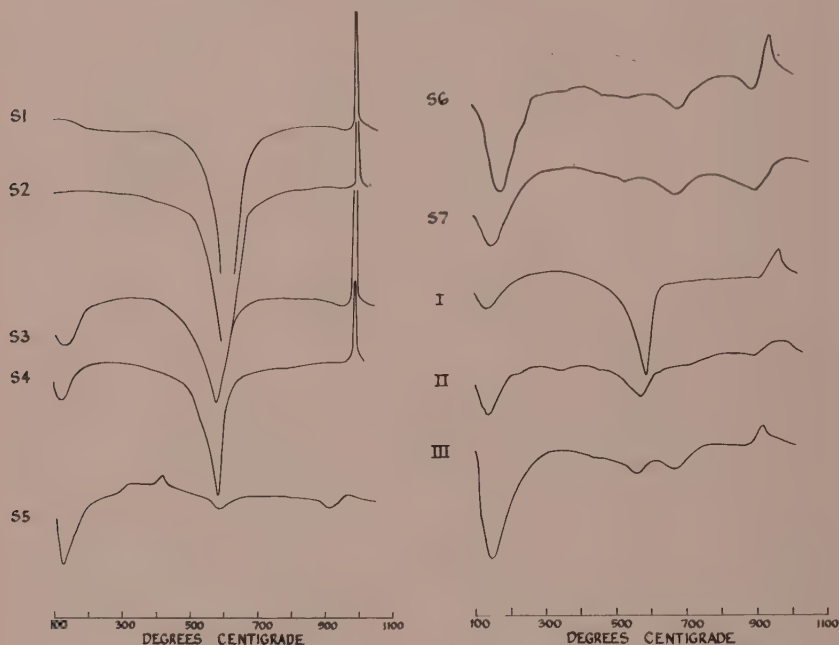


FIG. 1. Differential thermal analysis curves for reference minerals and natural clays. (See Tables 1 and 3).

persant, and then dried at 40° C. before being placed in a bromoform-alcohol solution of S.G. 2.00. A specific gravity of 2.27 was used for the recovery of the halloysite fraction.

DISCUSSION

The decrease in density (6) of the dried clay when treated with a bromoform alcohol solution is dependant on two factors. Firstly, the ability of the mineral to adsorb alcohol with a subsequent expansion of the lattice and, secondly, the particle size, which controls the specific surface of any given mineral. For montmorillonite and to a lesser extent halloysite, lattice expansion with the accompanying decrease in true

density is the predominating factor, but for kaolinite, illite and quartz, where expansion is insignificant, particle size is of greater importance. Consequently, the separation of montmorillonite and/or halloysite from mixed clay samples is possible by the technique outlined above, provided that other minerals occurring in the mixed samples do not have particles with diameters considerably smaller than the minerals being separated. The probability of this happening in the case of montmorillonite is remote, but with halloysite there is a strong possibility of one of the contaminants having such a particle size. In this event the value of the technique is doubtful.

ACKNOWLEDGMENTS

The author is indebted to Graeme T. See, B.Sc. for the chemical analyses.

REFERENCES

1. SPEIL, S. (1945), Applications of thermal analyses to clays and aluminous minerals: *U. S. Bur. Mines Tech. Paper* **664**, 1-37.
2. CARTHEW, A. R. (1955), Quantitative estimation of kaolinite by differential thermal analysis: *Am. Mineral.*, **40**, 107-117.
3. MACEWAN, D. M. (1946), Identification and estimation of montmorillonite group of clay minerals with special reference to soil clays: *J. Soc. Chem. Ind. (London)*, **65**, 298-305.
4. BUEHRER, ROBINSON AND DEMING (1948), The mineral composition of the colloidal fraction of some South Western soils in relation to field behavior: *Soil. Sci. Soc. Am.*, **13**, 157-165.
5. BUZAGH, A. AND SZEPESTI, K. (1955), Colloidal chemical determination of montmorillonite content in bentonite: *Acta Chem. Hung.*, (**3-4**), 287-298.
6. GRIM, R. (1953), Clay Mineralogy: pp. 312-314, McGraw Hill Book Co.

CHARACTERIZATION OF β -Ga₂O₃ AND ITS ALUMINA ISOMORPH, θ -Al₂O₃*

J. A. KOHN, GERALD KATZ AND J. D. BRODER, *Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey.*

ABSTRACT

Considerable disagreement exists in the literature on the question of whether or not the many varieties of alumina represent discrete phases. It has previously been shown that the high-temperature form of gallia (β) is isostructural, and forms a complete solid solution series, with θ -alumina. Lath-shaped crystals of β -Ga₂O₃, of sufficient size for single-crystal x -ray diffraction studies, have been grown from the vapor phase and were studied by optical and x -ray techniques. A twinned morphology was established, the true unit cell being monoclinic:

$$\begin{array}{ll} a_0 = 5.80 \pm 0.01 \text{ \AA} & \beta = 103^\circ 42' \\ b_0 = 3.04 \pm 0.01 \text{ \AA} & Z = 4 \\ c_0 = 12.23 \pm 0.02 \text{ \AA} & \text{Space Group} = A2/m \end{array}$$

All crystals examined were multiply twinned on (001), resulting in an apparent orthorhombic diffraction symmetry.

The cell dimensions of the isostructural alumina phase (θ) are contracted by approximately 3%. The characterization of β -Ga₂O₃ as a discrete crystallographic phase establishes θ -Al₂O₃ as a distinct polymorph of alumina. This lends support to the belief that other forms of alumina may well be represented by discrete crystalline phases.

INTRODUCTION

Many varieties of alumina are reported in the literature. The nature of these phases and their interrelationships are still unsettled issues (1). One group of investigators favors a type of order-disorder sequence (2) or a relationship involving crystallite size (3). A second school (4,5,6) interprets the various x -ray diffraction patterns as arising from a number of discrete crystalline phases. The major reported varieties of alumina include α -(corundum; hexagonal) (7), β -(containing Na (8), K (8), Mg (9), Ca (10), or Ba (11); hexagonal), γ -(cubic (12), tetragonal or orthorhombic (5)), δ -(orthorhombic) (5), κ -(orthorhombic) (5), η -(cubic, spinel type) (5), θ -(hexagonal) (13), χ -(approximately cubic) (5), and ζ -Al₂O₃ (Li₂O-containing; cubic) (14,15). A complete compilation of the known forms of alumina and hydrated alumina is given by Russell *et al.* (16).

Striking analogies have been observed between the oxides of aluminum and gallium. These are to be expected owing to the similarity between the two elements, both chemically and with respect to atomic radii. As a result, an extensive series of solid solutions (4,17) can exist between

* Presented at the Fourteenth Annual Pittsburgh Diffraction Conference, Pittsburgh, Pa., Nov. 1, 1956.

the stable, isomorphous alumina and gallia end members. The reported varieties of gallia include α -(hexagonal) (18), β -(non-cubic) (18), γ -(cubic) (19), δ -(body-centered cubic) (20), ϵ -(non-cubic) (20), Na₂O- or K₂O-containing-(hexagonal) (6), and Li₂O-containing-Ga₂O₃ (cubic) (6).

Unfortunately, the lack of systematic nomenclature among the alumina and gallia phases has in some cases confused the obvious parallelism between the two series. The following isomorphous pairs have been reported in the literature: α -Al₂O₃ and α -Ga₂O₃ (18), β -Al₂O₃ and the corresponding alkali-containing-Ga₂O₃ phases (6), γ -Al₂O₃ and γ -Ga₂O₃ (19), κ -Al₂O₃ and ϵ -Ga₂O₃ (4), θ -Al₂O₃ and β -Ga₂O₃ (6), and ζ -Al₂O₃ and Li₂O-containing-Ga₂O₃ (6).

The present study is concerned with a characterization of the unit cell and space group of β -Ga₂O₃ (the so-called high-temperature gallia) and consequently, its alumina isomorph, θ -Al₂O₃. The isomorphism of these two phases has been based upon their analogous x-ray powder patterns (6) and a complete solid solution between the two end members (4). However, no conclusive crystallographic characterization of this isostructural pair has yet been reported.

PREPARATION OF β -Ga₂O₃

The crystals of β -Ga₂O₃ used in the present study were prepared during the growth of gallium phosphide from excess gallium. Elemental phosphorus and gallium were sealed in an evacuated silica tube (25 μ Hg), held at 1100° C. for three hours, and slow-cooled at approximately 40° C./hr. The reaction product consisted of GaP crystals (major phase) and a minor amount of lath-shaped, light-blue crystals, the latter having formed on the tube wall in a cool region above the melt level. The minor-phase crystals, later shown to be β -Ga₂O₃, were formed from the vapor phase, probably by a reaction of gallium with residual oxygen. Spectrochemical analysis of the β -Ga₂O₃ crystals revealed minor amounts of Fe, Ca, Cu, Mg, Si and In; the latter element possibly imparted the light-blue color.

The high affinity of gallium for oxygen was clearly shown in another experiment: Elemental gallium was heated to 1100° C. in a stream of nitrogen. The light-grey, finely-fibrous reaction product consisted entirely of β -Ga₂O₃, as shown by x-ray powder patterns. The oxygen impurity in the nitrogen was apparently sufficient to oxidize the gallium.

β -Ga₂O₃ was also formed by heating elemental gallium in a quartz crucible at 700–800° C. in air. A surface layer of oxide, which readily formed over the molten gallium, inhibited oxidation, necessitating frequent agitation to insure a complete reaction. X-ray powder patterns showed the light-grey, finely-crystalline reaction product to be β -Ga₂O₃.

Stoichiometry

The light-blue crystals obtained from the first preparation method described above and the reaction products from the last two techniques were shown to be the same phase by *x*-ray powder diffraction. Furthermore, the pattern of this phase was found to be in good agreement with the powder data for β -Ga₂O₃ published by Roy *et al.* (20). The stoichiometry was confirmed by gain-in-weight measurements made in conjunction with the aforementioned direct heating of elemental gallium in air. A further confirmation of the stoichiometry was obtained from direct chemical analysis (21). Two determinations for Ga gave 74.48% and 74.73%. The average 74.61% compares favorably with the theoretical amount for Ga₂O₃, namely 74.41%.

UNIT CELL AND SPACE GROUP

The lath-shaped crystals of β -Ga₂O₃ were first examined with a polarizing microscope. They were found to be anisotropic, with parallel extinction when viewed normal to the lath axis, i.e., normal to either the face or edge of the lath. This implies either tetragonal, hexagonal, orthorhombic, or monoclinic symmetry. In the first two instances, it is further required that the *c* axis be coincident with the lath direction. The latter, in case of monoclinic symmetry, is coincident with the *b* axis for all practical purposes.

Interfacial angles around the lath direction were measured with a two-circle optical goniometer. The values obtained ($\sim 53^\circ$ and 76°) were inconsistent with uniaxial symmetry. Thus either orthorhombic or monoclinic symmetry is indicated for β -Ga₂O₃.

The optical findings were in apparent agreement with the results obtained using the precession and Weissenberg techniques. Preliminary interpretation of these diffraction patterns indicated an orthorhombic unit cell of the following dimensions:

$$\begin{aligned}a_0 &= 5.80 \pm 0.01 \text{ \AA} \\b_0 &= 3.04 \pm 0.01 \text{ \AA} \\c_0 &= 23.76 \pm 0.02 \text{ \AA}\end{aligned}$$

On the basis of this unit cell, the following absences were noted on the single-crystal patterns:

$$\begin{aligned}hkl \text{ with } h+l &\neq 2n \text{ (B-face centering)} \\h_{2n}k_{2m}l \text{ with } h+l &\neq 4n \\h_{2n}k_{2m+1}l \text{ with } h+l &= 4n\end{aligned}$$

These absences were not consistent with any orthorhombic space group. Accordingly, the remaining symmetry possibility, monoclinic, was considered.

It is known that orthorhombic symmetry can be derived from monoclinic symmetry by twinning. Accordingly, a closer examination was made of the lath-shaped crystals under high magnification, and the presence of reentrant angles typical of twinning was noted. The photomicrograph reproduced in Fig. 1 offers a view of the serrated or saw-

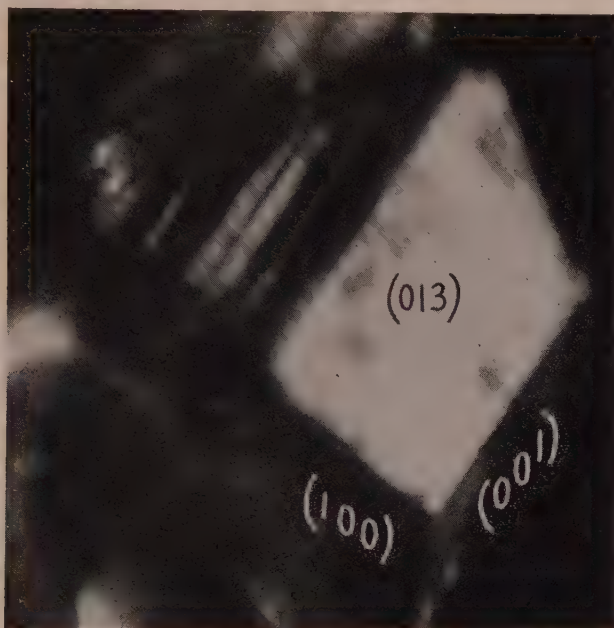


FIG. 1. Photomicrograph of a typical $\beta\text{-Ga}_2\text{O}_3$ crystal. The faces are indexed after the monoclinic unit cell. The zone of reentrant angles lies in $\{0kl\}$. (570 \times).

toothed zone. It will be recalled from the optical findings (see above) that, in case of monoclinic symmetry, the b -axis is coincident with the lath direction. The latter is essentially vertical in the photomicrograph. The composition plane of the proposed twin contains the lath direction, and therefore the b -axis, and consequently is of the type $(h0l)$.

Assuming the twin plane to be (001), the $(h0l)$ reciprocal lattice shown in Fig. 2 was constructed. The relationship between orthorhombic and monoclinic symmetry is apparent. The observed reflections have been indexed using the orthorhombic and both (normal and twinned) monoclinic unit cells. Considering only the normal (lower) monoclinic cell, it was found that the observed absences ((hkl) with $k+l \neq 2n$) were consistent with the space group $A2/m$. All observed reflections were accounted for by the composite lattice constructed from both monoclinic

cells. Thus the true symmetry is monoclinic, with the apparent orthorhombic symmetry deriving from polysynthetic twinning on (001). The monoclinic cell derived from single-crystal data is described as follows:

$$\begin{aligned} a_0 &= 5.80 \pm 0.01 \text{ \AA} & \beta &= 103^\circ 42' \\ b_0 &= 3.04 \pm 0.01 \text{ \AA} & \text{Space group} &= A2/m \\ c_0 &= 12.23 \pm 0.02 \text{ \AA} \end{aligned}$$

Using a measured density of 5.95 g/cm^3 (22), 4.02 formula weights per

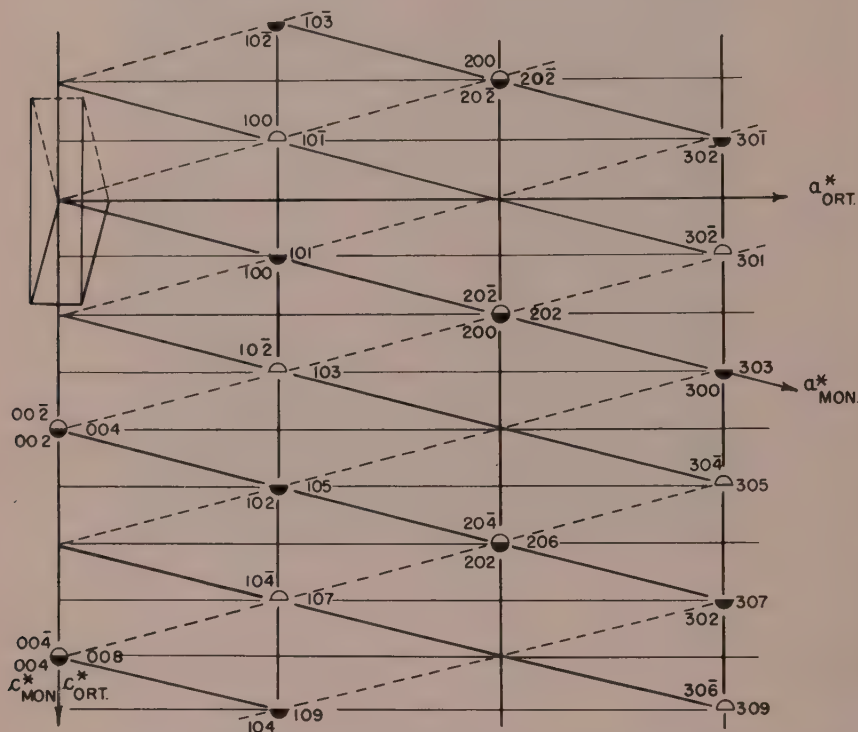


FIG. 2. Portion of the β - Ga_2O_3 reciprocal lattice showing the relationship between monoclinic and orthorhombic symmetry. Upper monoclinic cell (dashed) lattice points (open symbols) are indexed to the upper left of each permissible lattice site; lower monoclinic cell (solid, heavy) lattice points (solid symbols) are indexed to the lower left; orthorhombic unit cell (solid, light) lattice points are indexed to the right.

unit cell were calculated. The transformation matrix from orthorhombic to monoclinic indices is

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1/2 & 0 & 1/2 \end{vmatrix}$$

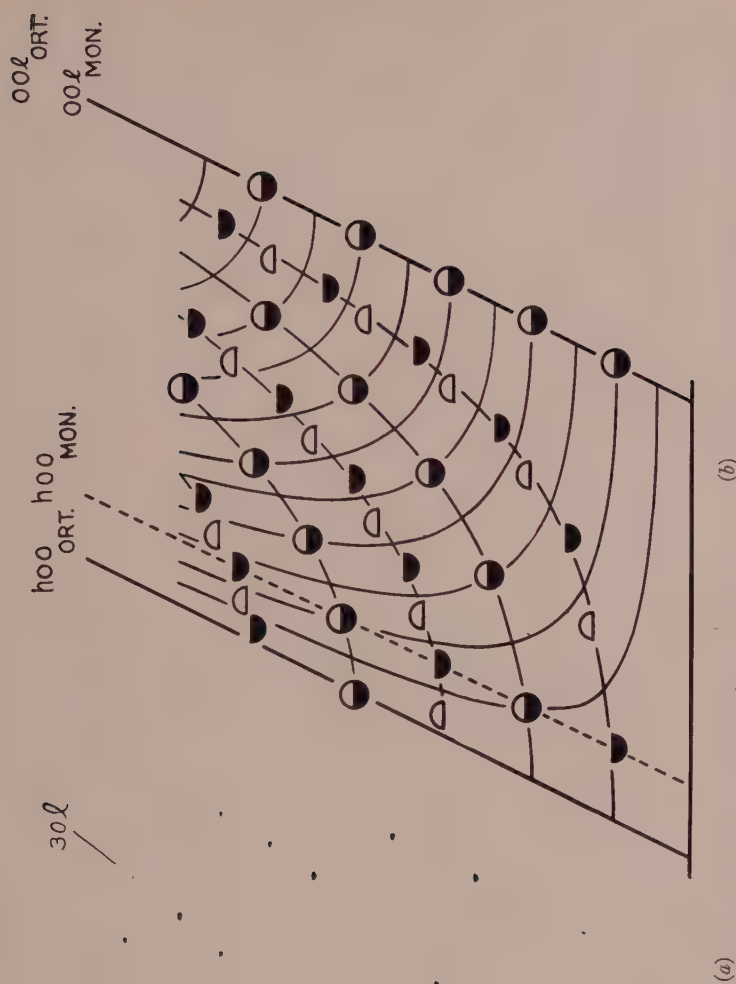


FIG. 3. (a) Portion of the $\beta\text{-Ga}_2\text{O}_3$ b-axis zero-level Weissenberg pattern. (b) Schematic interpretation of (a) (cf. Fig. 2 for explanation of symbols).

$\beta\text{-Ga}_2\text{O}_3$			$\theta\text{-Al}_2\text{O}_3$					
Ortho- rhombic <i>hkl</i>	Monoclinic		$d_{\text{obs.}} \text{ \AA}$	<i>I</i>	$d_{\text{obs.}} \text{ \AA}$ (5)	<i>I</i>	Tertian's Hexagonal Cell (2)	
	<i>hkl</i>	$d_{\text{calc.}} \text{ \AA}$					$d_{\text{calc.}} \text{ \AA}$	<i>hkl</i>
1 0 1	1 0 0	5.63	5.60	W+	5.25	W		
1 0 $\bar{3}$	1 0 $\bar{2}$	4.68	4.65	M	4.55	M	4.55	0 0 \cdot 3
1 0 5	1 0 2	3.68	3.66	W	3.56	VW	3.64	2 0 \cdot 0
0 0 8	0 0 4	2.970	2.967	VS	2.87	MS	2.84	2 0 \cdot 3
1 0 $\bar{7}$	1 0 $\bar{4}$	2.930	2.924	VS				
2 0 2	2 0 0	2.817	2.816	VS	2.74	MS		
1 1 $\bar{1}$	1 1 $\bar{1}$	2.675	2.673	M	2.58	W		
1 1 3	1 1 1	2.549	2.547	VS	2.45	MS		
1 0 9	1 0 4	2.403	2.396	S	2.325	M		
1 1 $\bar{5}$	1 1 $\bar{3}$	2.343	2.344	S	2.26	M	2.27	0 0 \cdot 6
1 1 $\bar{7}$	1 1 $\bar{3}$	2.110	2.103	M	2.03	MS	2.02	3 1 \cdot 0
2 1 0	2 1 $\bar{1}$	2.098						
1 0 $\bar{11}$	1 0 $\bar{6}$	2.024	2.020	M—				
0 0 12	0 0 6	1.980	1.978	M+	1.92	MW	1.927	2 0 \cdot 6
2 1 4	2 1 1	1.979						
0 1 10	0 1 5	1.872	1.869	M	1.81	W	1.818	4 0 \cdot 0
2 0 10	2 0 4	1.838	1.835	W+				
3 0 $\bar{5}$	3 0 $\bar{4}$	1.791	1.791	W	1.745	VVW		
1 0 13	1 0 6	1.743	1.737	W				
1 1 11	1 1 5	1.685	1.678	W+	1.625	VW		
3 0 $\bar{7}$	3 0 $\bar{2}$	1.680						
3 1 1	3 1 $\bar{1}$	1.628	1.626	VW				
3 1 $\bar{3}$	3 1 $\bar{3}$	1.598	1.598	M	1.55	M	1.543	2 2 \cdot 6
3 0 $\bar{9}$	3 0 $\bar{6}$	1.560	1.561	W+				
3 1 5	3 1 1	1.543	1.542	M	1.495	MW	1.508	3 1 \cdot 6
1 0 $\bar{15}$	1 0 $\bar{8}$	1.528	1.527	M				
0 2 0	0 2 0	1.520	1.521	W	1.461	MW		
0 0 16	0 0 8	1.485	1.479	M	1.435	VVW	1.424	1 1 \cdot 9
0 1 14	0 1 7	1.482						
0 2 4	0 2 2	1.473	1.450	W+	1.41	M	1.420	4 0 \cdot 6
4 0 0	4 0 $\bar{2}$	1.450						
1 2 $\bar{3}$	1 2 $\bar{2}$	1.446	1.439	VS	1.395	S	1.400	3 3 \cdot 0
2 1 12	2 1 5	1.440						
1 0 17	1 0 8	1.359	1.353	M, Br.				
0 2 8	0 2 4	1.353						
1 2 $\bar{7}$	1 2 $\bar{4}$	1.349	1.337	M—	1.293	W		
2 2 2	2 2 0	1.338						
3 1 $\bar{11}$	3 1 7	1.302	1.301	M—	1.265	VW		
4 1 2	4 1 $\bar{1}$	1.301						

TABLE 1. (continued)

$\beta\text{-Ga}_2\text{O}_3$			$\theta\text{-Al}_2\text{O}_3$				
Ortho- rhombic <i>hkl</i>	Monoclinic		$d_{\text{obs.}} \text{ \AA}$	<i>I</i>	$d_{\text{obs.}} \text{ \AA}$ (5)	<i>I</i>	Tertian's Hexag- onal Cell (2)
	<i>hkl</i>	$d_{\text{calc.}} \text{ \AA}$					$d_{\text{calc.}} \text{ \AA}$ <i>hkl</i>
1 2 9	1 2 4	1.285	1.283	M—	1.235	VW	
3 0 15	3 0 6	1.225					
1 0 $\overline{19}$	1 0 $\overline{10}$	1.222	1.222	W	1.188	?	
3 1 13	3 1 5	1.217					
			1.210	VW	1.161	VVW	
			1.169	VW	1.113	VW	
			1.159	VW—			
			1.146	M			
			1.133	W+			
			1.098	W	1.069	VVW	
			1.089	VW			
			1.076	W+	1.041	VW	
			1.060	VW, Br.			
			1.050	W+			
			1.043	VW	1.015	W	
			1.033	M, Br.	1.001	W	
			1.017	W			
			1.013	W+, Br.	0.977	VW	
			0.988	M	0.957	VW	
			0.976	VW			
			0.964	VW	0.938	VW	
			0.953	VW			
			0.945	VVW	0.919	VVW	
			0.937	W	0.910	VVW	
			0.930	W, Br.	0.893	VW	
			0.909	W, Br.			
			0.895	W, Br.			
			0.891	W+			
			0.881	W+	0.857	VVW	
			0.871	W+, Br.			
			0.861	M—	0.84	VVW	
			0.845	W	0.825	MW	
			0.843	W			
			0.836	M—			
			0.829	M			
			0.818	W+			
			0.815	W			
			0.798	M—			
			0.796	W			
			0.789	M—			
			0.784	M—			
			0.775	M			

A portion of the *b*-axis zero-level Weissenberg pattern is reproduced in Fig. 3*a*. The schematic interpretation is presented in Fig. 3*b*, in which it can be seen that certain sets of reflections derive from the normal (lower) monoclinic cell, whereas others derive from the cell in twinned position. In particular, along the (30*l*) lattice row of Fig. 3*a*, the reflections alternate in character, every other one being visibly multiple. This demonstrates that the crystals consist of sections in twinned orientation sandwiched between portions in normal position. Depending on the relative masses of the two portions in a given crystal, the relative intensity of the set of reflections from one orientation should differ with respect to that from the other orientation. This effect has been noted, further substantiating the postulated twinned monoclinic morphology.

CHARACTERIZATION OF θ -Al₂O₃

Table 1 presents the powder diffraction data for both β -Ga₂O₃ and θ -Al₂O₃. The observed Ga₂O₃ reflections are indexed with respect to both orthorhombic and monoclinic unit cells. The *d*-spacings have been calculated and compared with observed values. Isomorphism of the two compounds permitted direct indexing of the Al₂O₃ pattern. The cell dimensions of θ -Al₂O₃ are contracted with respect to those of its Ga₂O₃ isomorph by approximately 3%. The only other cell listed for θ -Al₂O₃ is one of hexagonal symmetry ($a_0 = 8.40$ Å, $c_0 = 13.65$ Å) given by Tertian (13), who reported obtaining crystals of this phase by calcining monocrystals of hydrated alumina. Using Tertian's cell, Ervin (2) calculated the *d*-spacings listed in Table 1. It will be noted that these spacings do not account for all the lines of the observed single-phase powder pattern, especially four rather prominent reflections between 2.325 and 2.74 Å.

It has been demonstrated by the foregoing evidence that β -Ga₂O₃ is a distinct crystalline phase, characterized by a specific unit cell. Its alumina isomorph, θ -Al₂O₃, with which it forms a complete solid solution series, has thus been identified as an equally discrete phase of alumina. This characterization of θ -Al₂O₃ lends credence to the belief that other varieties of alumina, as well as gallia, might similarly be described as equally discrete crystalline phases.

ACKNOWLEDGMENTS

The authors are grateful to Mr. R. Lefker, Signal Corps Engineering Laboratories, who made use of an IBM 650 for the spacing calculations, and to Mr. L. Toman, also of these Laboratories, for the photomicrograph.

REFERENCES

1. FRARY, F. C., *Ind. Eng. Chem.*, **38**, 129-31 (1946).
2. ERVIN, G., *Acta Cryst.*, **5**, 103-8 (1952).
3. JELLINEK, M. H., AND FANKUCHEN, I., *Ind. Eng. Chem.*, **37**, 158-63 (1945); **41**, 2259-65 (1949).
4. ROY, R., HILL, V. G., AND OSBORN, E. F., *Ind. Eng. Chem.*, **45**, 819-20 (1953).
5. STUMPF, H. C., RUSSELL, A. S., NEWSOME, J. W., AND TUCKER, C. M., *Ind. Eng. Chem.*, **42**, 1398-1403 (1950).
6. FOSTER, L. M., AND STUMPF, H. C., *J. Am. Chem. Soc.*, **73**, 1590-5 (1951).
7. PAULING, L., AND HENDRICKS, S. B., *J. Am. Chem. Soc.*, **47**, 781-90 (1925).
8. BEEVERS, C. A., AND BROHULT, S., *Z. Krist.*, **95**, 472-4 (1936).
9. BRAGG, W. L., GOTTFRIED, G., AND WEST, J., *Z. Krist.*, **77**, 255-74 (1931).
10. LÄGERQVIST, K., WALLMARK, S., AND WESTGREN, A., *Z. anorg. Chem.*, **234**, 1-16 (1937).
11. ADELSKÖLD, V., *Arkiv Kemi, Mineral. Geol.*, **12A**, No. 29, 9 pp. (1938).
12. KÖNIG, H., *Naturwissenschaften*, **35**, 92-3 (1948).
13. TERTIAN, R., *Compt. rend.*, **230**, 1677 (1950).
14. KORDES, E., *Z. Krist.*, **91**, 193-228 (1935).
15. BRAUN, P., *Nature*, **170**, 1123 (1952).
16. RUSSELL, ALLEN S., *et al.*, *Technical Paper No. 10*, Alcoa Research Laboratories, Aluminum Company of America, Pittsburgh, Pennsylvania (1956).
17. HILL, V. G., ROY, R., AND OSBORN, E. F., *J. Am. Ceram. Soc.*, **35**, 135-42 (1952).
18. GOLDSCHMIDT, V. M., BARTH, T., AND LUNDE, G., *Skrifter Norske Videnskaps-Akad.*, Oslo, I., *Mat. Naturv. Klasse*, No. 7, 24 (1925).
19. BÖHM, J., *Angew. Chem.*, **53**, 131 (1940).
20. ROY, R., HILL, V. G., AND OSBORN, E. F., *J. Amer. Chem. Soc.*, **74**, 719-22 (1952).
21. SCHWARZKOPF Microanalytical Laboratory, Woodside 77, New York
22. LUNDELL, G. E. F., AND HOFFMAN, J. I., *J. Res. Nat. Bur. Standards*, **15**, 409 (1935).

Manuscript received November 16, 1956.

SENGIERITE FROM BISBEE, ARIZONA

C. OSBORNE HUTTON, *Stanford University, California.*

ABSTRACT

The hydrated copper uranyl vanadate, sengierite, has been recognized as efflorescent patches on chalcocite from Cole Shaft, Bisbee, Arizona. It occurs as very minute greenish-yellow rhombic platelets, tabular parallel to (001); $\alpha=1.77, \pm 0.01$, $\beta=1.935$, $\gamma=1.960$, $\gamma-\alpha=0.190$; $2V=38^\circ (-)$. X-ray diffraction powder patterns correspond almost exactly with that yielded by type material from the Belgian Congo. Copper and uranium were detected by microchemical methods but calcium appears to be absent.

INTRODUCTION

Recently Mr. Scott Williams of Scottsdale, Arizona, very kindly brought to the writer's attention some specimens of chalcocite on the outer surfaces of which are pockets of radioactive greenish-yellow efflorescences tentatively identified as tyuyamunite. However, Mr. Williams' keen sense of observation led him to the conclusion that the color of the mineral in question was rather distinct from that of tyuyamunite, hence an investigation was made, the outcome of which is reported here.

The specimens studied were selected from a small collection purchased by Mr. Williams from Mr. William P. Crawford, now retired, but formerly Superintendent of Mines at Bisbee, Arizona, who in turn discovered the material about November of 1935, some 25 ft. above the 1100 ft. level in a small pod of massive chalcocite with which was associated minor amounts of malachite. I am grateful to Mr. Williams and Mr. Crawford for these data and also for the following information relating to the occurrence and environment of sengierite: "Sengierite occurred in one of a series of five sulfide-oxide veins which extended from the 800 ft. level to the 1300 ft. level of the Cole Shaft. The veins were in a very compact limestone of the Escabrosa Series. The richest part of the sulfide ore body containing the sengierite was between the 1000 ft. and the 1100 ft. levels. The ore was a mixture of chalcocite, covellite, malachite, with pockets of cerargyrite, and it assayed 35% copper and 250 oz. of silver per ton. Uranium mineralization was present in the limestones as tyuyamunite which occurred as small yellow crystals lining cracks and fissures in the limestone country rock adjacent to the massive chalcocite-covellite ore bodies. Above the 1000 ft. level the ore-bearing vein (containing sengierite) turned to oxide ore (primarily malachite, azurite, and clay). The copper and silver values ran out at the 800 ft. level. The area was mined out and abandoned in 1940."

Optical and x-ray diffraction studies of the mineral in question have shown conclusively that it is sengierite, and therefore, this is the first

record of this mineral in the United States; the only other occurrences are at Haut-Katanga, Belgian Congo (Vaes and Kerr, 1949, Donnay and Donnay, 1955), and the Argana Bigoudine Region, Morocco (Chervet and Branche, 1955, pp. 90-91).

MINERALOGY

Sengierite occurs in small pockets and patches up to 20 mm. in diameter, as quite minute rhombic-shaped platelets, the longer diagonals of which do not exceed 0.03 mm., but average less than 0.02 mm. This simple rhombic outline is due to the dominance of the unit prism and the crystals are tabular parallel to the basal plane. In some crystals small faces bevel the acute angles of these platelets, and rare crystals exhibit re-entrant angles, possibly due to twinning.

The color is yellow with a greenish tinge. Refractive indices have been determined by means of white phosphorus-sulphur liquids, since high refractive arsenical liquids reacted immediately with sengierite modifying color to brownish-green and at the same time refractive indices changed most noticeably. The following data were determined: $\alpha=1.77$, ± 0.01 , $\beta=1.935$, $\gamma=1.960$, $\gamma-\alpha=0.19$. It was most difficult to determine the least refractive index with accuracy owing to the habit of the mineral, and the value reported should be considered less accurate than the other data. Basal plates do not appear to be pleochroic but for the mineral generally X =colorless to very palest greenish-yellow, Y =greenish-yellow, Z =greenish-yellow, with absorption $Z=Y>X$. A very low birefringence and strong anomalous interference tints are pronounced for basal sections; this is the preferred orientation of crystals of sengierite in liquid mounting media. Satisfactory interference figures were not obtained from the minute crystals but Fedorov stage measurements gave $2V=38^\circ$, $\pm 3^\circ$, with negative optic sign; $r<v$.

X-ray diffraction data for Bisbee, Arizona sengierite (column 1) are shown in the accompanying Table 1 and it will be noted that the similarity between these data and those for sengierite from the Belgian Congo (column 2) is very close indeed, and almost the sole discrepancy is the definite absence of the strong reflection at 3.179 Å in the writer's films of Bisbee material; an explanation for this circumstance is not clear. Further it should be noted that there is a very fine splitting of the lines at 9.80 Å and 4.91 Å and although specimens were prepared in several ways with considerable care, this effect, which may be due to absorption, could not be avoided.

Although insufficient material was available for quantitative analytical work, microchemical tests showed that copper and uranium are present; calcium appears to be absent.

TABLE 1. X-RAY DIFFRACTION POWDER PATTERNS OF SENGIERITE

Camera diameter 114.59 Å. Radiation $\text{CuK}\alpha=1.5418 \text{ Å}$

<i>hkl</i>	1		2		3	
	<i>d. (Obs.) Å</i>	<i>I</i>	<i>d. (Obs.) Å</i>	<i>I</i>	<i>d. (Obs.) Å</i>	<i>I</i>
001	9.80	10	9.82	v.v.st.	9.883	10
—	—	—	—	—	6.566	1
11 $\bar{1}$	5.72	2	5.75	m	5.736	1
111	5.02	1	5.02	w	—	—
002	4.91	9	4.91	v.st.	4.915	10
201	4.175	3	4.179	m	4.160	2
020	4.035	4	4.037	m	4.020	3
021	3.73	6	3.735	st.	3.710	3
003	3.26	<1	3.262	w	—	—
202	3.21	6	3.197	st.	—	—
22 $\bar{1}$	—	—	3.179	st.	—	—
220,	—	—	—	—	—	—
310,	022	3.15	7	3.144	st.	3.153
—	11 $\bar{3}$	3.10	7	3.094	st.	—
—	312	2.96	3	2.970	m	2.951
—	221	2.91	<1	2.901	v.w.	—
—	311	2.839	2	2.832	m	2.836
—	113	2.739	1	2.744	w	2.721
13 $\bar{1}$,	023	2.556	4	2.550	m	2.549
322,	131	2.500	<1	2.495	v.w.	—
—	312	2.435	3	—	2.433	3
—	213	—	—	2.398	w	—
—	214	2.349	<1	2.345	v.w.	—
—	231	2.269	<1	2.267	v.w.	2.252
420,	322	2.165	<1	2.163	w	—
—	330	2.126	3	2.124	m	2.128
402,	033	2.089	3	2.087	m	2.086
—	51 $\bar{1}$	2.053	1	2.051	w	2.052
—	423	2.013	4	2.009	m	2.001
41 $\bar{4}$,	14 $\bar{1}$	1.973	1	1.971	v.w.	—
115,	215	1.952	<1	1.951	v.w.	—
015,	43 $\bar{1}$	1.900	<1	1.898	v.w.	—
—	24 $\bar{1}$	1.877	2	1.881	w	—
—	432	1.848	3	1.850	w	1.857
—	125	1.806	<1	1.808	v.w.	1.802
602,	433	1.758	4	1.756	m	1.760
61 $\bar{1}$,	043	1.721	3	1.724	v.w.	1.715
—	423	1.6665	3	1.666	v.w.	1.667
—	006	1.634	<1	1.637	v.w.	1.632
—	342	1.587	1	1.586	v.w.	1.588
—	126	1.553	<1	1.553	v.w.	—
144, 251,	344	1.511	<1	1.509	v.w.	1.508
—	534	1.496	<1	1.495	v.w.	—

1. Cole Shaft, Bisbee, Arizona.

2. Haut-Katanga, Belgian Congo (Donnay and Donnay, 1955, pp. 23–26).

3. Haut-Katanga, Belgian Congo (Vaes and Kerr, 1949).

N.B. Additional lines can be recognized in the film of Bisbee, Arizona, sengierite, but they are too weak and diffuse to measure with acceptable accuracy.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Mr. Scott Williams, Scottsdale, Arizona, for bringing the sengierite specimens to my attention, and to

Mr. William P. Crawford for his assistance in supplying notes on occurrence. To Miss Daphne D. Riska, U. S. Geological Survey, Washington, D.C., I am much indebted for her willingness to compare my films with those obtained from Belgian Congo material. Professor E. Wm. Heinrich, University of Michigan, kindly drew my attention to the occurrence of sengierite in Morocco.

REFERENCES

- CHERVET, J., AND BRANCHE, G. (1955), Contribution a l'étude des minéraux secondaires d'uranium Français: *Ann de l'École Nat. Supér. de Géol. Appl. et de Prosp., Min. de l'Univ. de Nancy*, **3**, 1-2, pp. 1-186; esp. pp. 90-91.
- DONNAY, G., AND DONNAY, J. D. H. (1955), Contribution to the crystallography of uranium minerals: *U. S. Geol. Surv.*, **TEI-507**, *U. S. Atomic Energy Commission, Tech. Inf. Service*, Oak Ridge, Tenn., pp. 1-42.
- VAES, J. F., AND KERR, P. F. (1949), Sengierite: A preliminary description: *Am. Mineral.*, **34**, 109-120.

Manuscript received Sept. 12, 1956.

NOTES AND NEWS

PARAGENESIS OF ANTHOPHYLLITE AND HORNBLLENDE FROM THE BANCROFT AREA, ONTARIO

C. E. TILLEY

There are few records in the literature of the paragenesis anthophyllite-hornblende which have been presented in detail, and I can call to mind only one association which has been the subject of quantitative chemical study. Such is the anthophyllite-tremolite paragenesis of Edwards, St. Lawrence, Co., N. Y., though to judge from the published analytical data of several workers, further study of material of undoubted purity from this locality is still required.

The paragenesis of anthophyllite and cummingtonite on the other hand has been closely investigated in a number of examples and it may be inferred that this association of amphiboles is of commoner occurrence than the one noted above.

Eskola (1950) and Seitsaari (1952) have more recently discussed the association of cummingtonite and hornblende in assemblages from Finland and their studies provide the first quantitative investigation of this particular paragenesis.


In the present note a chemical study is presented of the anthophyllite-hornblende association from an assemblage from near Bancroft, Ontario.

The assemblage in question is a foliated metagabbro forming a facies of the large Mallard Lake gabbro mass of Dungannon Township in Hastings County, Ontario, at a point $\frac{3}{4}$ mile East of York River Bridge on the East Road out of Bancroft. The north end of this metagabbro intrusion has been mapped by Hewitt in Carlow Township and it is known to extend southwest as far as Egan Chute on the York River near York River Bridge (Hewitt, 1955). The rock is a schistose metagabbro of medium grain size, rich in black hornblende, conspicuous clove brown needles of anthophyllite reaching a quarter of an inch in length, and plagioclase. Under the microscope the constituents are seen to be green hornblende, light colored anthophyllite, both minerals appearing in independent idioblastic crystals, plagioclase, and as accessories magnetite and apatite. The approximate mode (wt. per cent) is hornblende 65, anthophyllite 10, plagioclase 23, iron ore and apatite 2.

The plagioclase has a composition An_{45} and is not conspicuously twinned or zoned. Of the amphiboles, green hornblende is dominant and shows frequently in longitudinal section conspicuous striation or parting

parallel to (001). The anthophyllite forms striking elongated prisms piercing green hornblende aggregates, and though homoaxial growths are recorded they are quite subordinate.

The optical characters of the two amphiboles are summarized below.

Green hornblende: α 1.653, β 1.665, γ 1.675, $2V_{\alpha}80^{\circ}$ 
 $\gamma \wedge c$ 19° , $\beta = b$

Pleochroism marked— α greenish yellow, β green, γ bluish green
 Absorption $\beta > \gamma > \alpha$.

Anthophyllite: α 1.649, β 1.656, γ 1.665, $2V_{\gamma}78^{\circ}$
 $\gamma = c$, $\beta = b$

Pleochroism feeble— α and β colorless to palest yellow, γ smoke grey.
 Absorption $\gamma > \beta = \alpha$.

The rock and the two separated amphiboles have been subjected to analysis by Mr. J. H. Scoon, the results being presented in Table 1.

The analysis of the rock is distinguished by its low value of potash, but the assemblage presents the chemical features of an olivine gabbro and in Table 2 (columns 1 and 2) is compared with the average olivine gabbro computed by Nockolds (1954).

The amphibole analyses are given in Table 1 (columns 2 and 3), the analysis of the anthophyllite being corrected in column 3(a) for the estimated two per cent impurity of hornblende which remained in the anthophyllite fraction after repeated treatment in heavy liquids in the isodynamic separator.

In Table 2 analyses of chemically comparable amphiboles are set down, the compared anthophyllite of Montana being associated with cummingtonite (Rabbitt, 1948).

When we contrast the anthophyllite and green hornblende of the Ontario metagabbro we note that the hornblende is more highly aluminous and has larger amounts of Fe_2O_3 , TiO_2 , Na_2O and K_2O in its structure, a feature also revealed in the hornblende member associated with cummingtonite in the Finnish assemblages described by Eskola (1950) and Seitsaari (1952).

It is of interest to set out the relative distribution of magnesium and iron in studied paragenetic amphiboles, and for this purpose the ratio

$$mg = \frac{\text{Mg}}{\text{Mg} + \text{Fe}^{+3} + \text{Fe}^{+2} + \text{Mn}} \text{ (atom)}$$

is recorded for the following associations.

TABLE 1

	1	2	3	3(a)	Norm of 1	Metal atoms to 24 (O, OH, F, Cl)
SiO ₂	46.52	43.82	50.07	50.06	Or 0.28	Si 6.351 } 2 7.203 } 3
Al ₂ O ₃	16.77	14.85	7.45	7.28	Ab 24.89	Al 1.649 } 8.00 0.797 } 8.00
Fe ₂ O ₃	2.66	3.32	1.01	0.96	An 32.53	Al 0.874 } 0.445 0.365 } 0.103
FeO	9.44	11.15	18.33	18.42	Hi 0.06	Fe''' 1.348 } 5.32 Fe'' 0.035 } 0.069
MnO	0.22	0.27	0.56	0.57	Di 9.24	Mn 0.078 } 0.026 0.627 } 3.968
TiO ₂	1.24	0.68	0.21	0.20	Hy 4.82	Ti 2.627 } 1.583 0.504 } 2.10
MgO	9.54	12.07	18.33	18.40	Ol 20.21	Ca 0.017 } 2.225 0.017 } 2.24
CaO	9.04	10.20	1.06	0.87	Il 2.28	OH 1.879 } 0.017 F 0.017 } 1.90
Na ₂ O	3.02	1.79	0.78	0.76	Mt 3.71	Cl 0.009 } 0.017
K ₂ O	0.05	0.12	0.02	0.02	Ap 0.34	
H ₂ O+	1.59	1.94	2.32	2.32	Fl 0.12	
H ₂ O-	0.06	0.06	0.08	0.08	Rest 1.65	
F	0.04	0.04	nil	nil	100.13	
Cl	0.04	0.03	0.06	0.06		
P ₂ O ₅	0.16					
Less O =F, Cl	100.39 0.03 100.36	100.34 0.03 100.31	100.28 0.03 100.25	100.00		Sp. Gr. 3.21 3.22

1. Anthophyllite-hornblende metagabbro (Mallard Lake), East Road, $\frac{3}{4}$ mile E of York River bridge, 6.7 miles East of Bancroft, Ontario.
2. Hornblende of metagabbro, 3 Anthophyllite of metagabbro, 3(a) Anthophyllite, analysis 3 recalculated after removal of 2 per cent of hornblende (analysis 2).

A=Anthophyllite, C=Cummingtonite, H=Hornblende

A	C	H	Reference
0.60	0.59	—	Sundius (1933)
0.41	0.47	—	Eskola (1936)
0.61	0.30	—	Rabbitt (1948)
	0.70	0.76	Eskola (1950)
	0.40	0.33	Seitsaari (1952)
0.62	—	0.60	Mallard Lake metagabbro

Here we note that in the case of the anthophyllite-cummingtonite associations the most striking disparity in *mg* values is seen in the Montana paragenesis (Rabbitt 1948) but the full description of this association is apparently not yet available. Omitted from the table are the *mg* values of the analyses of anthophyllite (gedrite) and cummingtonite recorded by Collins (1942) from Sutherland, for these analyses are from rocks each containing only one of the amphiboles.

TABLE 2

	1	2	3	4	5	6
SiO ₂	46.52	46.83	50.06	50.36	43.82	44.23
Al ₂ O ₃	16.77	17.38	7.28	8.06	14.85	14.62
Fe ₂ O ₃	2.66	1.91	0.96	2.18	3.32	5.11
FeO	9.44	8.20	18.42	18.26	11.15	8.94
MnO	0.22	0.14	0.57	nil	0.27	0.21
TiO ₂	1.24	0.97	0.20	0.43	0.68	1.81
MgO	9.54	10.03	18.40	17.57	12.07	10.78
CaO	9.04	11.36	0.87	0.74	10.20	10.81
Na ₂ O	3.02	2.03	0.76	0.70	1.79	1.51
K ₂ O	0.05	0.40	0.02	nil	0.12	0.61
H ₂ O+	1.59	0.63	2.32	1.69	1.94	1.42
H ₂ O—	0.06	—	0.08	—	0.06	0.08
P ₂ O ₅	0.16	0.12	—	—	—	—
F	0.04	—	nil	nil	0.04	0.22
Cl	0.04	—	0.06	—	0.03	—
	100.39	100.00	100.00	99.99	100.34	100.35

1. Anthophyllite-hornblende metagabbro (analysis 1, Table 1).
2. Average olivine gabbro (Nockolds, 1954, p. 1020).
3. Anthophyllite (Analysis 3(a), Table 1).
4. Anthophyllite from amphibolite (cummingtonite-bearing) Madison Co., Montana (Rabbitt, 1948, p. 270).
5. Hornblende (analysis 2, Table 1).
6. Hornblende from hornblende schist, Glen Tilt, Perthshire (Deer, 1938, p. 68).

Values of *mg* are closely comparable for the anthophyllite-hornblende pair of the Mallard Lake metagabbro, but are contrasted in the cummingtonite-hornblende pair described from Finland.

As has been emphasized by Eskola it will be useful to have further amphibole parageneses quantitatively investigated, for their chemical variation may well prove sensitive indicators of the conditions under which these metamorphic assemblages have crystallized.

REFERENCES

- COLLINS, R. S. (1942), Cummingtonite and gedrite from Sutherland: *Mineral Mag.*, **26**, 254-259.
- DEER, W. A. (1938), The composition and paragenesis of the hornblendes of the Glen Tilt Complex, Perthshire: *Mineral. Mag.*, **25**, 56-74.
- ESKOLA, P. (1936), A paragenesis of gedrite and cummingtonite from Isopää in Kalvola, Finland: *Bull. Comm. Geol. Finlande*, **115**, 475-487.
- (1950), Paragenesis of cummingtonite and hornblende from Muuruvesi, Finland: *Amer. Min.*, **35**, 728-734.
- HEWITT, D. F. (1955), Geology of Montegale and Carlow Townships: *Ann. Report Ont. Dept. Mines*, LXIII, Pt. 6 (1954), 12-14.
- NOCKOLDS, S. R. (1954), Average chemical compositions of some igneous rocks: *Bull. Geol. Soc. America*, **66**, 1007-1032.
- RABBITT, J. C. (1948), A new study of the anthophyllite series: *Amer. Min.*, **33**, 263-323.
- SEITSAARI, J. (1952), Association of cummingtonite and hornblende: *Annal. Acad. Sci. Fenn.*, Ser A, III, **30**, 1-20.
- SUNDIUS, N. (1933), Ueber die Mischungslücken zwischen Anthophyllit-Gedrit, Cummingtonit-Grünerit und Tremolit-Aktinolith: *Mineral. und Pet. Mitt.*, **43**, 422-440.

PREPARATION OF PETROGRAPHIC SECTIONS WITH BONDED DIAMOND WHEELS

HENRY N. BAUMANN, JR., *Carborundum Company, Niagara Falls, N. Y.*

INTRODUCTION

The preparation of thin sections of rocks and minerals for petrographic examination was ably presented in 1953 by Read and Mergner (1) who summarized the development of thin-sectioning techniques together with a detailed description of the established practice of the U. S. Geological Survey. In recent years, the methods of petrography have become increasingly useful in ceramics and other non-metallic and refractory technology. Recently Insley and Frechette (2) have published a comprehensive work in this field of industrial petrography. In many instances standard methods for preparing thin sections may be applied to ceramic microscopy, but there is an increasing number of articles or materials to which they can be applied with only partial effectiveness

or not at all. Included among these are grinding wheels, other abrasive articles, super refractories of silicon carbide and other compounds, and ceramic articles such as sintered alumina products.

Bonded diamond wheels were introduced into industry about twenty years ago, specifically for grinding and dressing sintered carbide tool points. For a number of years before bonded diamond wheels were available, the Research and Development Laboratory of the Carborundum Company at Niagara Falls, N. Y., had repeatedly attempted unsuccessfully to make thin sections of vitrified bonded silicon carbide grinding wheels. It was suggested that diamond wheels be tried for this purpose, and after a number of trial runs using laps of different grits, and grade designation, a method of making such sections was successfully developed. Bonded diamond wheels were at first made only with resinoid bonds and consequently wheel life was short and the use of the wheels proved to be costly. As new and better types of bonded diamond wheels were produced, the process of sectioning bonded abrasives, loose abrasive grain, and special refractories has become routine procedure in the petrographic laboratories of several manufacturers of abrasive and special refractory products. The metal bonded diamond wheels are now effectively and economically employed and resinoid wheels used little or not at all. Vitrified diamond wheels may also be used, and although they have good grinding efficiency, they are slower cutting than the metal wheels.

EQUIPMENT AND WHEEL SPECIFICATIONS

The equipment generally employed for preparing thin-sections with loose silicon carbide grain uses large iron disks of the order of twelve inches in diameter for lapping. In the use of bonded diamond wheels we have found wheels of six inch diameter to be most economical. For further economy and also for convenience in mounting we have a one inch diameter recess countersink in the center, the center itself is a $\frac{1}{4}$ drill hole through which is placed the bolt for mounting.

While commercially available polishing equipment such as is widely used in metallography may be adapted to the preparation of thin sections, we, like many other petrographic laboratories, have built our own lapping machines. Fig. 1 is a close-up view of thin sectioning equipment in the mineralogical laboratories of the Research Laboratory of the Carborundum Company in Niagara Falls, N. Y. It is possible to make sections successfully with a single machine because wheels may be changed rapidly, and there is no danger that a loose coarse grain from an early stage will be retained to contaminate and ruin the section in a later stage. The apparatus shown is provided with a means of varying the speed between 500 and 1500 RPM. In preparing thin sections the higher speed

is used, but the equipment is adaptable to other methods of specimen preparation such as polishing, where slower speeds are required.

TECHNIQUE OF PREPARING SECTIONS

In preparing thin sections with bonded diamond wheels the same principles apply as when loose grain is used. A slice of the order of $\frac{1}{16}$ to $\frac{1}{8}$ inch thick is cut from the sample. In our laboratory, we use a Felker



FIG. 1. Close-up of bonded diamond wheel in use. Note the special slide holder, and the freely flowing stream of water.

Manufacturing Company Model 11R cutting-off machine equipped with a rotary table and vise, and on which a Carborundum Co. MI8695H-8 $\times 0.45 \times \frac{5}{8}$ inch metal bonded diamond cutting-off wheel is mounted.

The slice is placed on a glass object slide with Canada balsam, after first polishing one face for the final mount. Many petrographers develop their own methods for mounting sections, and a particular procedure for abrasive articles is described by the author in the section on Abrasive

Microscopy in the Insley and Frechette manual for the Microscopy of Ceramics and Cements (2). This mounted section is then ground to its proper thickness in stages using the following order of wheels, first 100 grit, then 240 and finally a 400 grit lap. At times a 600 grit wheel is used, especially for a polished face (3). During the operation of grinding the section a full stream of warm water should be used in order to keep the specimen and mounting medium from spalling and also to minimize loading of the wheel, but the water should not be so warm that the balsam would soften. The wheel is occasionally dressed with lump pumice, chiefly to keep the wheel from loading with the mounting medium. Occasionally, it may be dressed with a vitrified bonded stone such as is provided by diamond wheel manufacturers for dressing wheels used in grinding sintered carbide tools. In handling the mounted specimen, it should be moved radially in such a manner as to minimize dishing of the surface. Figure 1 shows the manner in which the specimen should be held.

We have attempted unsuccessfully up until now to use bonded silicon carbide laps for making thin sections of materials on the order of hardness of quartz. The abrasive action of rolling loose grain is quite different from that of bonded abrasives with fixed abrasives points. The success of bonded diamond lap is the great hardness of diamonds compared with all other crystalline materials. Wooddell (4) has shown by his method of hardness rating that on a scale on which quartz is 7 and corundum is 9 (the ordinary Mohs' scale values), various types of diamond would be on of the order of 40 and silicon carbide would be 14. The bonded diamond grit cuts right through the crystals of the section without undercutting any of the softer bond or included structures.

While the subject method was designed primarily for the preparation of hard materials in the field of abrasives, refractories and ceramics, we have also found it economically applicable to the sectioning of the rocks and minerals. It has also been useful in preparing special materials; for example, thin sections of teeth and bone for biological studies. Thin sections of water soluble or water reactive materials such as calcium carbide have been successfully made using a layer of kerosene or some light oil on the surface as a coolant and lubricant instead of a stream of water. The chief disadvantage of this method is the first cost, but if properly bonded diamond laps are carefully used they should be economical, provided that the volume of work is sufficient.

The advantages of the preparation of thin sections with bonded diamond wheels are: (1) obtaining thin sections of material not otherwise possible to section, (2) cleaner sections since there is no loose grit to embed, (3) speed of the operation, (4) ease of learning the technique,

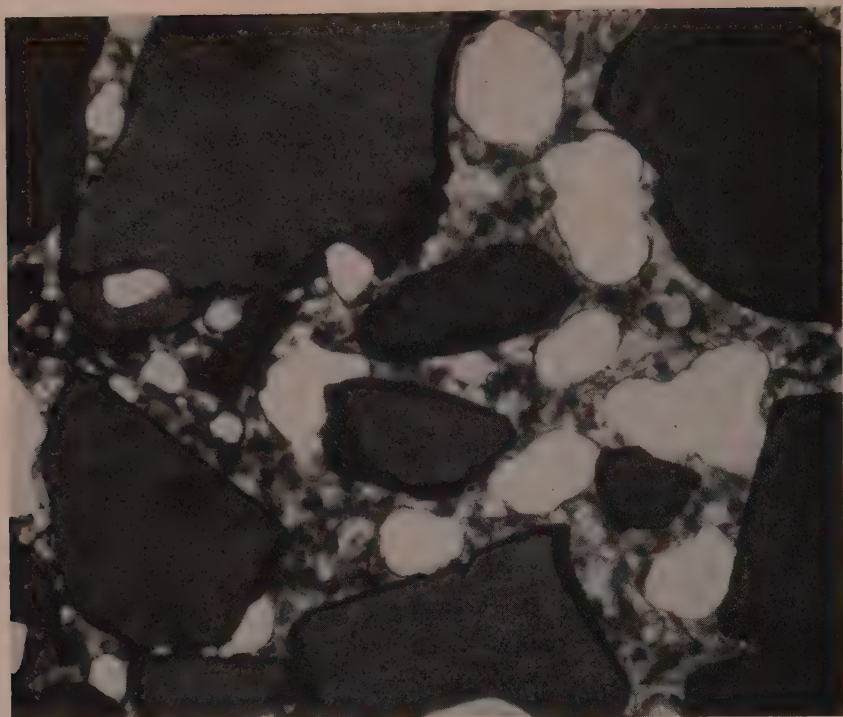


FIG. 2. Photomicrograph of a thin section of a vitrified bonded silicon carbide grinding wheel made with a bonded diamond wheel. $\times 71$, transmitted light.

(5) no undercutting of sections containing soft components such as the soft, porous bonds in some vitrified abrasive wheels.

Figure 2 is a photomicrograph of a section of a vitrified silicon carbide grinding wheel that can only be made with diamond abrasives.

The structure of the abrasive grain, the adhesion and other properties of the ceramic bond, and the shape and size of the pores can be observed.

Figure 3 is a photomicrograph of a thin section of a calcareous sandstone made by this method.

That the principles of petrography have been applied only in a limited way to the technology of ceramic products may be in part due to the difficulty of quickly obtaining thin sections. We have overcome this condition by the use of the equipment and procedures described above, and consequently petrography has become a regular technique for research, development and technical control in the abrasive and refractory industry.

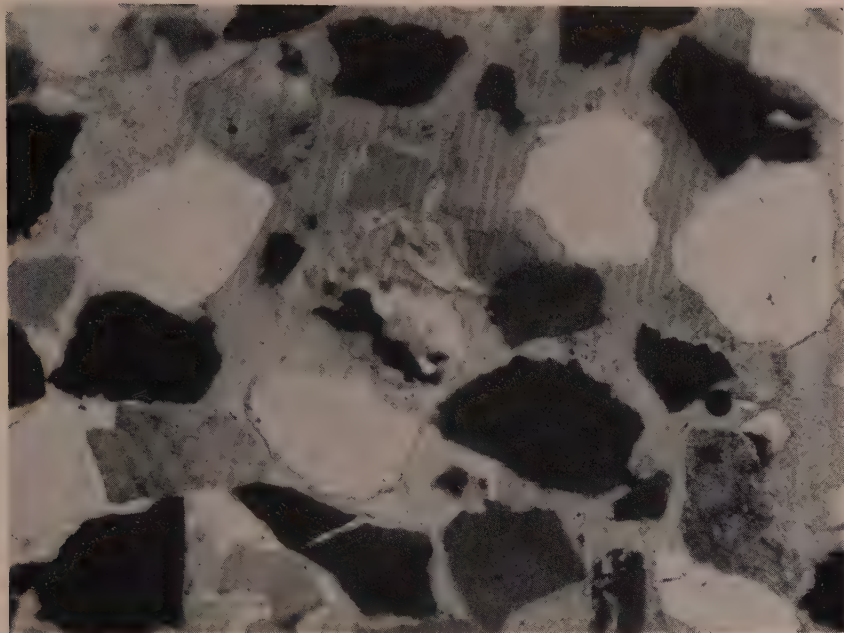


FIG. 3. Thin section of a calcareous sandstone made with a bonded diamond wheel.
 $\times 57$. Crossed nicols.

REFERENCES

1. FRANK S. REED AND JOHN L. MERGNER, The preparation of rock thin sections. *Am. Mineral.* **33**, 1184-1208 (1953).
2. HERBERT INSLEY AND VAN DERCK FRECHETTE, *Microscopy of Ceramics and Cements, Including Glass, Slags and Foundry Sands* (with a chapter on Abrasive by H. N. Baumann, Jr.) Academic Press, New York, N. Y. (1955).
3. The Carborundum Company designations for this series of metal bonded diamond wheels are:

61106C— $6 \times \frac{3}{4} \times \frac{5}{16}$ —D100-M50— $M_{\frac{1}{16}}$

61106C— $6 \times \frac{3}{4} \times \frac{5}{16}$ —D240-M50— $M_{\frac{1}{16}}$.

61106C— $6 \times \frac{3}{4} \times \frac{5}{16}$ —D400-M50— $M_{\frac{1}{16}}$.

61106C— $6 \times \frac{3}{4} \times \frac{5}{16}$ —D600-M50— $M_{\frac{1}{16}}$.

4. CHARLES E. WOODDELL, Methods of comparing hardness of electric furnace products and natural abrasives: *Trans. Electro Chem. Soc.*, **68**, 120 (1935).

TWO NEW TYPES OF HOLDERS USED IN GRINDING THIN SECTIONS¹

MANNING COCHRAN AND A. G. KING,² *U. S. Geological Survey, Denver, Colorado.*

Two highly satisfactory thin-section holders have been constructed and put into use. These help materially in the ease of preparing petrographic thin sections. The boron carbide holder used for coarse grinding has an automatic section-thickness control. This automatic control eliminates the many time-consuming inspection-correction steps during coarse grinding and assures a uniform product for finish grinding. The plastic holder used for finishing aids in handling the section on the lap. The slides are less likely to pull free when this holder is used than when the slides are hand-held. This results in less breakage. Both of these holders are inexpensive and their use does not require modification of pre-existing equipment.

BORON CARBIDE HOLDER

The holder is made of two blocks of aluminum joined by two $\frac{1}{4}$ -inch D stainless-steel pins so that one block is free to slide on the pins, while the other remains stationary (fig. 1). A rectangular depression machined from the center of the blocks accommodates a petrographic slide with its mounted chip. Two strips, $3 \times \frac{1}{2} \times \frac{3}{16}$ inch, are made from boron carbide wheel-dressing sticks. These strips are cemented with an epoxy cement into grooves in the top edges of the aluminum blocks. The top surfaces of the strips determine a plane, and the position of this plane with respect to the bottom of the depression (alignment platform) determines the over-all thickness of the slide. The sample cannot grind below this plane because the boron carbide is harder than the abrasives (emery or silicon carbide) used for lapping.

The over-all dimensions of the boron carbide holder are 3 inches long, 2 inches wide, and $\frac{3}{4}$ inch thick. The distance between the carbide top surface and the alignment platform is 0.060 inch for this particular holder. A small groove is milled out around the platform to facilitate precision alignment. The outside edges of the boron carbide strips are rounded to prevent them from gouging the lap surface.

The slide with its mounted rock chip is placed on the alignment platform. Both the platform and the back of the slide have to be clean to obtain the desired final thickness. The slide is held in the holder by sliding the movable block up against the slide edge. The slight finger

¹ Publication authorized by the Director, U. S. Geological Survey.

² Present address: 2-B Boyd St., Worcester, Mass.

pressure against the edges of the holder, as the slide is being ground, is sufficient to hold the section in place. The holder and sample are held against the revolving lap, which is charged with the grinding abrasive. As grinding progresses the boron carbide eventually comes in contact with the lap surface. If grinding is not perfectly parallel, one corner or edge will touch the lap first. Continued grinding of the sample corrects this wedging. No particular corrective measure need be taken on the

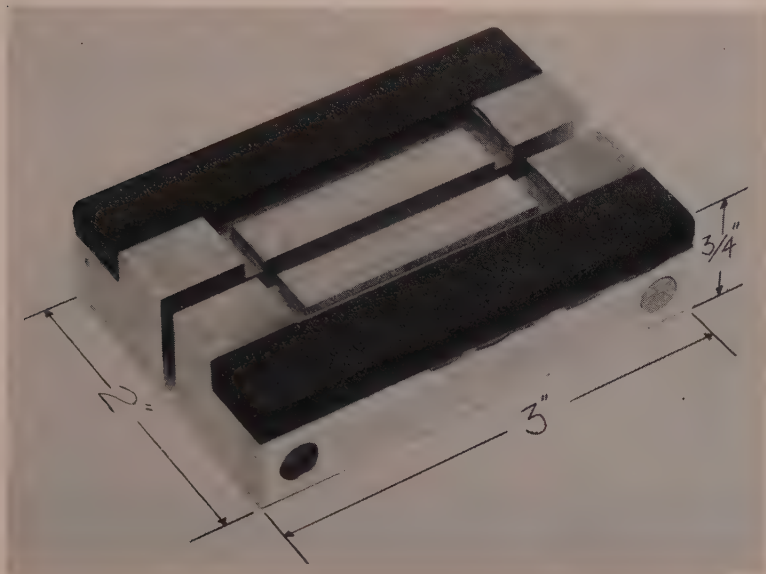


FIG. 1. Boron carbide holder.

part of the operator. The operator knows when the section is finished because of the increased drag of the holder on the lap surface. Doming of the rock section is also automatically corrected and the finished section, for this stage in the procedure, is planar, parallel, and has a uniform thickness. Tolerances are easily controlled to ± 0.0005 inch. The finished dimension of 0.060 ± 0.0005 inch is the sum of the glass, cement, and rock thicknesses. If irregularities occur in either the glass slides or in the cement, the thickness of the rock slice will be different from that expected. For this reason it is not considered practical to attempt finish grinding with this holder.

There have been difficulties in grinding two types of materials with this device: sandstones and ultramafic rocks. For sandstones it is customary in the laboratory to mount sandstone chips a little colder than

our usual samples. This results in an extra-thick layer of cement between the rock chip and the glass slide. The extra cement thickness causes the rock slice to be thinner after grinding when this holder is used but a holder with a lower alignment platform could be built to accommodate these samples. Ultramafic rocks are troublesome because they have a tendency to pluck during grinding. This characteristic requires more care in grinding than with other samples. A holder producing thicker sections would also partly solve this problem.

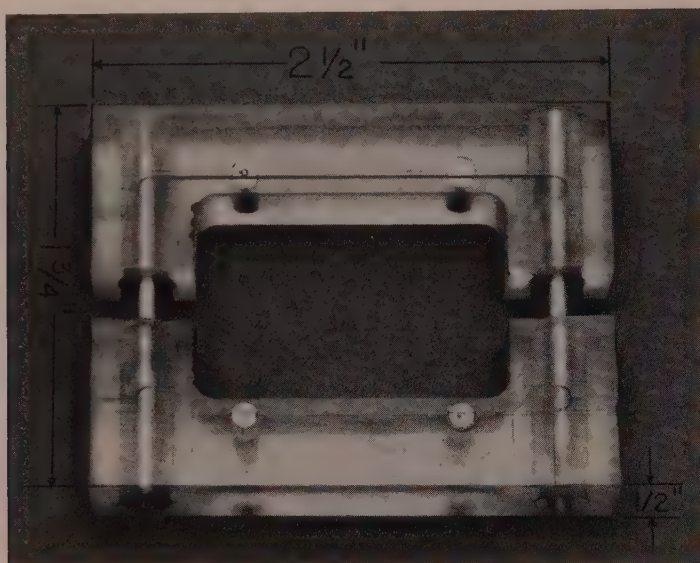


FIG. 2. Plastic holder.

PLASTIC HOLDER

After the sections have been ground with the boron carbide holder on the coarse abrasive they are ground to 30-micron thickness using a finishing holder. At present this procedure is accomplished in two grinding stages, using first 600 SiC, and next 303 $\frac{1}{2}$ emery. Preliminary results indicate that it will be possible to use an automatic thickness holder during the 600 SiC stage.

The plastic holder, Fig. 2, was machined from a block of methyl methacrylate plastic and has over-all dimensions of 2 $\frac{1}{2}$ inches long, 1 $\frac{3}{4}$ inches wide, and $\frac{1}{2}$ inch thick. The plastic block is in two pieces that slide on two $\frac{1}{4}$ -inch D stainless-steel pins. A rectangular hole, 1 $\frac{1}{2}$ by $\frac{3}{4}$ inches and centrally located, was cut out to allow microscopic examina-

tion of the section in process without removing it from the holder. In the place of the alignment platform, a shelf 0.03 inch deep, $1\frac{7}{8}$ inch long, and $\frac{1}{16}$ inch wide was milled into the edge of the rectangular hole to grip the slide. Four $\frac{1}{8}$ -inch D brass pins help in holding the section by preserving a sharp shoulder edge on this shelf.

The holder is used in much the same manner as the boron-carbide holder except that the thickness and uniformity are not controlled. During grinding the slide is periodically checked with a petrographic microscope in the conventional manner. The slide is not removed from the holder during inspection.

SUMMARY

The amount of skill required for the first grinding stage is less than that required when the thin section is processed in the conventional manner. The process is accelerated due to the elimination of many inspection steps during coarse grinding. Because a uniform section results from using the automatic thickness holder during coarse grinding, the finishing stage can be accomplished with less corrective measures. Holders used for finishing aid in ease of handling the sections as they are ground. Both of these holders have been used in practice and aid materially in the preparation of petrographic thin sections.

GENTHELVITE FROM COOKSTOVE MOUNTAIN, EL PASO COUNTY, COLORADO*

GLENN R. SCOTT, *U. S. Geological Survey, Denver, Colorado.*

In February 1951 a small but highly modified crystal of genthelvite $\text{Zn}_4\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$, (Fig. 1) was found on a northeast-trending spur of Cookstove Mountain in the $\text{NE}\frac{1}{4}\text{NW}\frac{1}{4}\text{NW}\frac{1}{4}$ sec. 4, T. 15 S., R. 67 W. (U. S. Geological Survey Manitou $7\frac{1}{2}$ -minute quadrangle), El Paso County, Colo. Another occurrence of genthelvite from El Paso County was recently reported (Glass and Adams, 1953), but because of the rarity of genthelvite, further discussion on the mode of occurrence and crystallography is thought to be warranted.

The genthelvite crystal was taken from a pegmatite in the Pikes Peak granite. The pegmatites on the northeast-trending spur of Cookstove Mountain crop out in a narrow north-northwest-trending belt that seems to be part of a larger system of pegmatite dikes. Three places along this north-northwest-trending system, that are well known to mineralogists

* Publication authorized by the Director, U. S. Geological Survey.

for the rare and well-crystallized minerals described in more than 40 articles since 1876, are St. Peter's Dome, Cookstove Mountain, and Crystal Park.

Several generalizations can be made about the structure and mineralogy of the pegmatite dikes in the dike system. The pegmatites in this system follow an arch-like joint structure described by Stevens (1949,

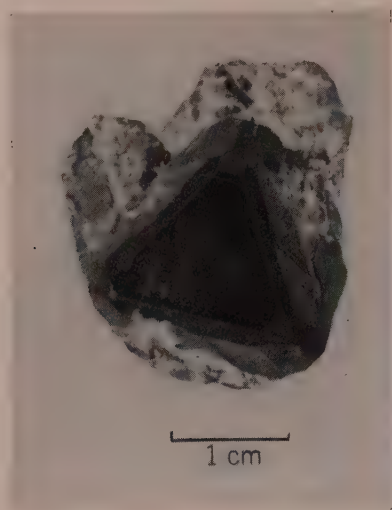


FIG. 1. Photograph of genthelvite crystal from El Paso County, Colo.; looking at the negative tetrahedral face ($\bar{1}\bar{1}1$), ($\times 1.55$).

p. 268) as his second group of joints. Individual dikes strike slightly west of north and dip gently to the east. Most of the dikes near St. Peter's Dome contain subhedral crystals that are tightly bound together or "frozen-in" with little or no intercrystal space. Very few of the pegmatite dikes in that area contain miarolitic cavities. Thorium-bearing minerals are common in the "frozen-in" dikes, but are rare in the miarolitic cavities. Toward the north, pegmatites with miarolitic cavities become more common and possibly make up one-half the total number of pegmatites around Fairview (Manitou quadrangle 1:48,000). Correspondingly, thorium-bearing minerals are rare and consist mostly of tabular crystals of metamict thorite in miarolitic cavities. The form of the thorite crystals suggests that they may have been the monoclinic variety huttonite. Topaz, phenakite, and amazon stone are rare near Fairview, but become more common north of Bear Creek and are most abundant at Crystal Park where the miarolitic cavities are larger. Con-

versely, "frozen-in" pegmatites are rare north of Bear Creek and thorium-bearing minerals are unknown to the author from the pegmatite dikes of that area.

The miarolitic cavities in the larger pegmatite dike system seem, from preliminary reconnaissance, to range in altitude from 7,600 feet to 9,000 feet above sea level. Within this vertical range near Fairview there are two broadly defined zones; the lower zone with pegmatites containing bastnaesite, siderite altered to hematite, quartz, microcline-perthite, zircon, huttonite(?), and columbite; and the upper zone with pegmatites containing bastnaesite, siderite altered to limonite, quartz, microcline-perthite, fluorite, topaz, phenakite, and genthelvite. Mineral deposition seems to have followed approximately the order in which the minerals are listed.

The pegmatite from which the genthelvite was taken is a collapsed miarolitic cavity 3 feet long, 6 inches wide at the widest part, and about 4 inches deep. The walls of the pegmatite consist of a 2-inch thick graphic intergrowth of quartz and microcline-perthite, set here and there with small, brown, opaque zircon crystals. Interstices in the walls are filled with limonite. Well-formed crystals of smoky quartz and microcline-perthite project from the walls. Penetrating them are crystals of bastnaesite and siderite altered to limonite. The genthelvite crystal was emplaced on a quartz-microcline-perthite-biotite intergrowth.

Most of the pegmatites in the upper zone contain fluorite; however, fluorite was not noted in either of the genthelvite-bearing pegmatites (Glass and Adams, *op. cit.*, p. 858). Another peculiarity of the two genthelvite-bearing pegmatites concerns the elongated form of the smoky quartz crystals (Adams, personal communication). The prism tapers very gradually to an almost microscopic pyramid. This type of quartz crystal has not been observed in any other pegmatite in the area.

The genthelvite crystal (Fig. 2) is a combination of the positive (*o*) and negative (*o*₁) tetrahedra, thus having the appearance of a slightly distorted octahedron. The crystal is further modified by the rhombic dodecahedron (*d*), the cube (*a*) (on the negative tetrahedral face only), the deltoid dodecahedron (*p*), the and trigonal tristetrahedron (*n*). One of the tetrahedral faces is dull and is sculptured parallel to the edges of the tetrahedral face; the other face is lustrous and unsculptured. The lustrous face was chosen arbitrarily as the negative tetrahedron for the purpose of this discussion. The length of the vertical axis is about 2.6 cm. and the lateral axes about 2.9 cm.

Crystallographic, chemical, and *x*-ray tests show that the crystal is unquestionably genthelvite. The negative tetrahedral faces of the crystal are grayish red, but the other faces are black. In transmitted light small

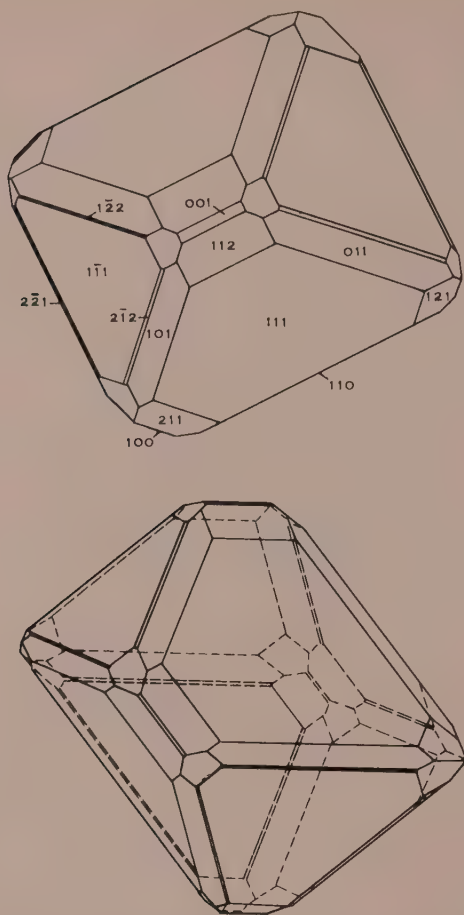


FIG. 2. Orthographic and clinographic projections of genthelvite crystal from El Paso County, Colo.

chips are pale pink. The fracture is uneven, the luster vitreous. The hardness is about 6.5.

The mineral is isotropic and transparent. The index of refraction $n = 1.745$.

Microchemical tests by J. W. Adams of the U. S. Geological Survey confirmed the presence of zinc, beryllium and sulfur.

An x -ray film prepared by R. P. Marquiss of the U. S. Geological Survey was compared by F. A. Hildebrand, also of the Survey, with the unit cell measurements of the original genthelvite sample from West

Cheyenne Canyon near St. Peter's Dome, El Paso County, Colo., and he finds that the unit cell measurements of the two correspond.

REFERENCES

- GLASS, J. J., AND ADAMS, J. W. (1953), Genthelvite crystal from El Paso County, Colorado: *Am. Mineral.*, **38**, 858-860.
- STEVEN, T. A. (1949), Geology and fluorspar deposits of the St. Peter's Dome district, Colorado: *Colo. Sci. Soc. Proc.*, **15**, no. 6, 259-284.

THE CRYSTALLOGRAPHY OF CERITE

P. GAY, *Department of Mineralogy and Petrology,*
Cambridge, England.

In a recent note (Glass, Evans, Carron and Rose, 1956) the crystallography of the rare earth silicate, cerite, from the Mountain Pass district of California has been described as monoclinic with cell dimensions $a = 17.81$, $b = 10.85$, $c = 14.10$ Å, $\beta = 109^\circ 10'$, and space group $I2/n$ or In . During the course of investigations of some rare earth silicates, the present author has examined a number of cerite specimens from the Mountain Pass and other localities. It has been found that all specimens are trigonal with slightly variable cell dimensions $a \sim 10.8$, $c \sim 37.7$ Å and probable space group $P312$, $P31m$ or $P\bar{3}1m$, etc. There is, however, a marked pseudocell in which the c -axis length is halved, giving a pseudo-space group $R32$, $R3m$ or $R\bar{3}m$; the true primitive cell is denoted by weak reflexions midway between the strong 19 Å layer lines on c -axis oscillation photographs.

It is of interest to see how these conflicting observations may be reconciled. Obviously the monoclinic b -axis is identical with the trigonal a -axis (i.e., $b_M = a_T$). If the trigonal description is correct it requires that in the (010) section of the monoclinic reciprocal net (Fig. 1) there shall exist two perpendicular row lines, along one of which the repeat distance is a_T^* and along the other the repeat is c_T^* ; this latter direction must be a triad symmetry axis. The angle $201_M \wedge \bar{1}01_M$ is exactly 90° and the dimensions are such that the 201_M face normal is the direction of a_T^* and the $\bar{1}01_M$ face normal is the direction of c_T^* (Fig. 1). The trigonal character of the $\bar{1}01_M$ direction may be confirmed by suitable x -ray photographs. Although the body-centered monoclinic description of the cerite lattice may be reconciled with a trigonal cell of the correct dimensions, it implies that the true lattice is not primitive but rhombohedral. In the present work, no detailed examination of the Mountain Pass cerite was

made; the poor quality single crystals obtained were used only to confirm the general features of the diffraction pattern known from the examination of cerites from other localities. The primitive character of the trigonal lattice was demonstrated by indexing oscillation photo-

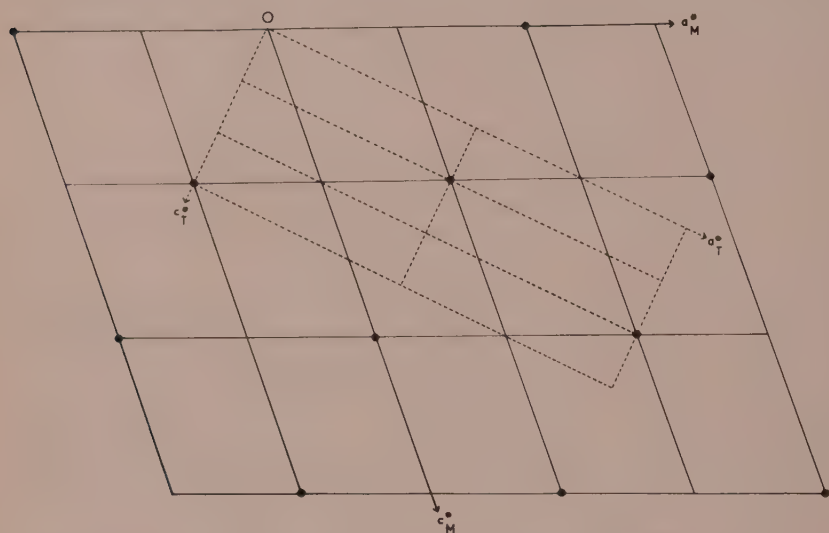


FIG. 1. (010) section of the monoclinic reciprocal net. Full lines denote the monoclinic lattice, dotted lines the trigonal lattice.

graphs of Swedish specimens. Nevertheless, it seems probable that the moving film methods employed by Glass *et al.* allowed the observation of only some of the weak true cell reflexions, whilst those denoting the primitive cell of the Mountain Pass specimen were undetected. The "octahedral" habit of the Mountain Pass cerite was ascribed by Glass *et al.* to the combination of the forms $\{100\}_M$, $\{011\}_M$ and $\{\bar{1}01\}_M$. These forms are plotted for holosymmetric monoclinic symmetry on the stereogram in Fig. 2. If this stereogram is rotated into the conventional trigonal orientation (i.e., with $\bar{1}01_M$ at the center of the projection), it can be seen that this "octahedral" habit is due to the relative development of the $\{0001\}$ pinacoid and the $\{\bar{1}012\}$ rhombohedron.

In the present work, cerite has always appeared optically uniaxial; it seems likely that the slight biaxial character recorded by Glass *et al.* must be regarded as anomalous. A new chemical analysis upon a cerite from Bastnäs, Sweden, has been carried out. This suggests a formula $(\text{Ca}, \text{Ln})_3 \text{Si}_2 (\text{O}, \text{OH}, \text{F})_9$, where Ln = lanthanon rare earths, with 20 or

21 formula units in the cell. The large cell dimensions prevent the unambiguous determination of Z .

Goddard and Glass (1940) suggested the existence of a series of cerites with variable lime contents. Some evidence in support of this suggestion

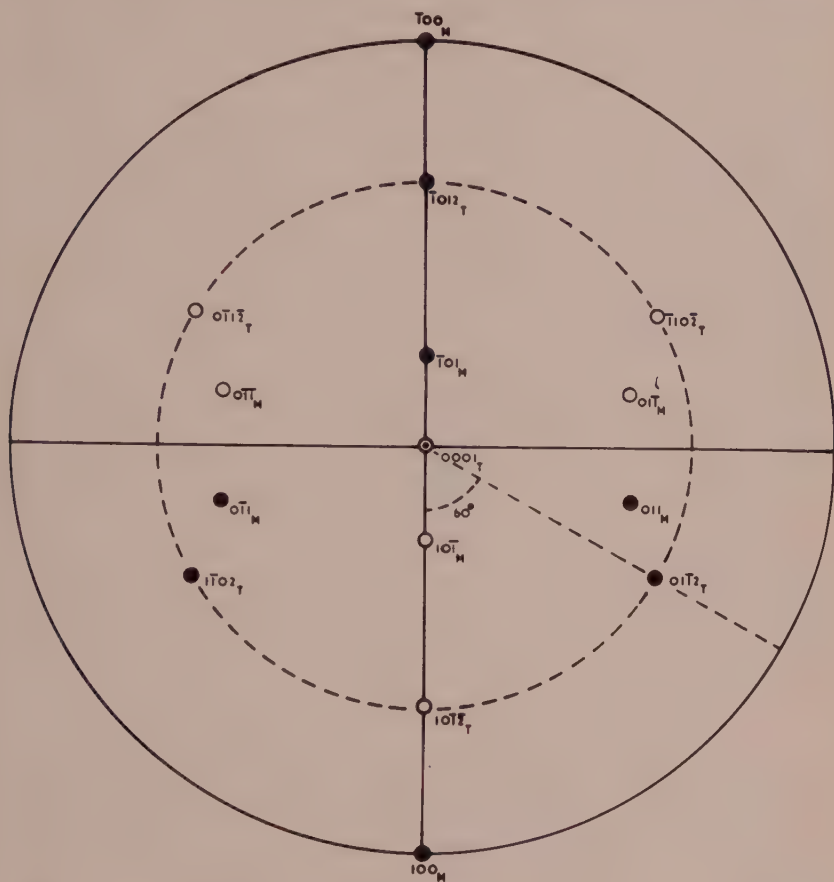


FIG. 2. Stereogram showing forms comprising the "octahedral" cerite crystals from Mountain Pass, California. Faces with subscript M denote position of monoclinic forms; faces with subscript T denote the positions of these poles after rotation of $\bar{1}01_M$ to the centre of the projection.

has been obtained. Apart from small cell dimension changes, the diffraction patterns from specimens from Bastnäs, Sweden, and Jamestown, Colorado, U. S. are similar except that the weak true cell reflexions are about twice as strong for the latter; chemically, the Colorado specimen

contains approximately twice as much CaO as the Bastnäs material. Thus, it might be expected that the hypothetical CaO-free cerite would have a rhombohedral lattice with $c \sim 18-19 \text{ \AA}$; the doubled c -axis of the primitive cell becomes more clearly developed as the lime content of the cerite increases. The effect of this lime content may be further studied by examination of the minerals lessingite and beckelite, which can be regarded chemically as lime-rich members of the cerite series. It is found that these two minerals have a structure different from that of cerite. Their diffraction patterns are very similar to each other and to that of the phosphorus-bearing mineral britholite, and indicate a structure dimensionally comparable with apatite. For a hexagonal cell, the dimensions are $a \sim 9.7 \text{ \AA}$, $c \sim 7.1 \text{ \AA}$, with probable space group $P6_3$ or $P6_3/m$. An idealized formula $(\text{Ca}, \text{Ln} \cdot \cdot \cdot)_2 (\text{Si}, \text{Al}, \text{P}) (\text{O}, \text{OH}, \text{F})_6$ is proposed for this series. Marked biaxial properties observed in some specimens suggest that the structure may be truly orthorhombic, with only a very close dimensional approximation to a hexagonal cell.

A full account of the work on these minerals, together with data for stillwellite, an unrelated silicate of the rare earths with boron, will be given in a paper to be published elsewhere.

The specimen of cerite from Mountain Pass, California, was kindly provided by Miss Jewell J. Glass (U. S. Geological Survey).

REFERENCES

- GLASS, JEWELL J., EVANS, HOWARD T., CARRON, M. K., AND ROSE, HARRY (1956). Cerite from Mountain Pass, San Bernardino County, California: *Am. Mineral.*, **41**, 665.
GODDARD, EDWIN N., AND GLASS, JEWELL J. (1940). Deposits of radio-active cerite near Jamestown, Colorado: *Am. Mineral.*, **25**, 381-404.

LINEATION PROTRACTOR*

LYNN MCINTOSH AND MELVIN E. HANES, *U. S. Geological Survey, Washington 25, D. C.*

A practical transparent protractor that is simple and easy to use has been designed to show relationships between lineation and the containing s -plane. The instrument consists of a standard 180° protractor to which has been added s -plane dip curves and a movable plunge indicator arm. The values for plotting the s -plane dip curves were derived from the formulas given in a paper by Ingerson and Tuttle (1943).

The protractor makes possible a quick solution of any one of the 4 variables when 3 are known. For example, in practice the strike and dip

* Publication authorized by the Director, U. S. Geological Survey.

of the *s*-plane and the trend (bearing) of lineation can be measured directly in the field; the plunge (the angle from the horizontal measured in the vertical plane) may then be obtained from the protractor. Other combinations of three directly measured factors may, of course, be used, depending on individual circumstances.

Figure 1 illustrates the instrument set for a lineation trend of 40° from

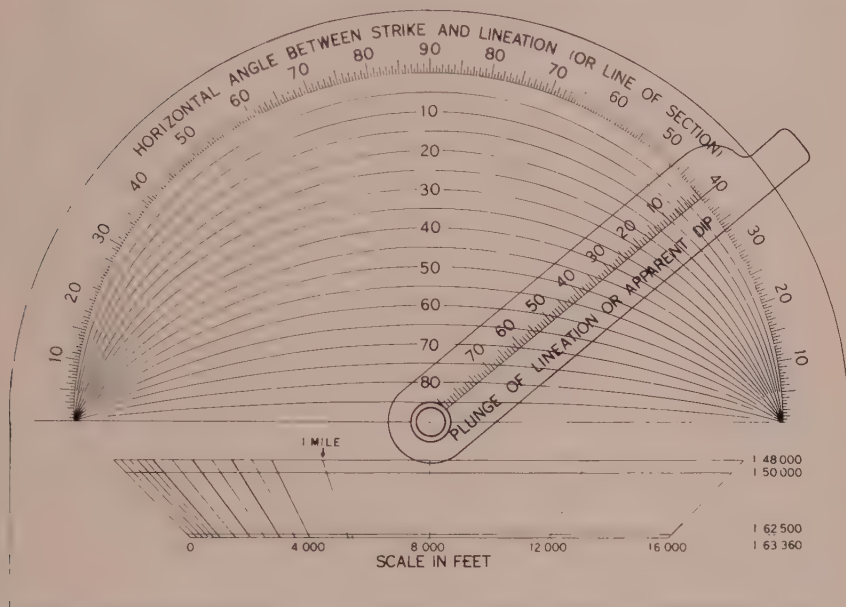


FIG. 1. Lineation protractor.

the strike of the containing *s*-plane. For this setting the lineation plunge is $48^\circ \pm$ for an *s*-plane that has a dip of 60° .

In constructing geologic cross sections, the protractor also may be used for finding apparent dip from true dip by considering the scale for horizontal angles to be equivalent to the angle between the strike and the line of the section. The apparent dip is then found on the indicator arm where it intersects the true dip curve. In this respect the lineation protractor is somewhat similar to the Wentworth (1917) dip protractor, the Wright (1916) geological protractor, and charts of other workers, but is easier to use than the earlier models.

The lineation protractor has been designed in two models—one for field use as shown in Fig. 1, and a larger size for office use by manuscript editors, compilers, and cartographers. Both models also contain a scale

diagram in feet for the commoner mapping scales. No plans have been made to produce the device in quantity for use outside the Geological Survey.

REFERENCES

- INGERSON, EARL, AND TUTTLE, O. F. (1943), A graph for determining angle and direction of pitch of lineation in the field: *Am. Mineral.*, **28**, 209-210.
WENTWORTH, C. K. (1917), A proposed dip protractor: *Jour. Geology*, **25**, 489-491.
WRIGHT, F. E. (1916), A geological protractor: *Wash. Acad. Sci. Jour.*, **6**, 5-7.

ANNUAL MEETING

The thirty-eighth annual meeting of the Mineralogical Society of America will be held in Atlantic City, New Jersey, Monday through Wednesday, November 4-6, 1957. Detailed notices will be mailed to all members.

Abstracts of papers to be presented at the annual meeting must be received by the Secretary on or before July 15, 1957. Abstract blanks may be obtained from the Secretary

NOMINATIONS OF OFFICERS FOR 1958

- President:* George E. Goodspeed, University of Washington, Seattle 5, Washington.
Vice-President: Ralph E. Grim, University of Illinois, Urbana, Illinois.
Secretary: C. S. Hurlbut, Jr., Harvard University, Cambridge, Massachusetts.
Treasurer: Earl Ingerson, U. S. Geological Survey, Washington, D. C.
Editor: Lewis S. Ramsdell, University of Michigan, Ann Arbor, Michigan.
Councilors (1958-1960): Richard H. Jahns, California Institute of Technology, Pasadena, California.
Charles Milton, U. S. Geological Survey, Washington, D. C.

The 7th Annual Convention of the Gulf Coast Association of Geological Societies will be held at the Roosevelt Hotel, New Orleans, Louisiana, on November 6-8, 1957.

The Sixth National Clay Conference will be held at the University of California in Berkeley, August 19-23.

The five-day program will include a field trip, two full sessions devoted to clay genesis, one to clay-liquid systems, and one to general subjects.

For information and enrollment write to the Dept. of Conferences and Special Activities, University of California Extension, Berkeley 4, California.

BOOK REVIEWS

STRUCTURE REPORTS FOR 1940-1941. Vol. 8. General Editor, A. J. C. Wilson; Section Editors: N. C. Baenziger (Metals), J. M. Bijvoet (Inorganic Compounds), J. Monteath Robertson (Organic Compounds). Published for the International Union of Crystallography by N. V. A. Oosthoek's Uitgevers Mij., Utrecht, Holland, viii+384 pp. (1956). Price 80 Dutch florins; alternatively may be purchased from Polycrystal Book Service, 84 Livingston St., Brooklyn 1, N. Y., \$21.50.

With the publication of Volume 8, the gap between the last volume of *Strukturbericht* (Vol. 7, 1939) and the new *Structure Reports* is filled. Beyond an expression of appreciation to the editors for their great contribution to crystallography, this latest volume requires no special comment. Crystallographers the world over are already familiar with these indispensable reports.

R. M. DENNING

University of Michigan, Ann Arbor, Michigan

AN INTRODUCTION TO CRYSTALLOGRAPHY. By F. C. PHILLIPS, pp. viii plus 324, 515 illustrations, Longmans, Green and Company, New York, Second Edition, 1956. Price \$6.00.

The second edition of this book was called for because of the enthusiastic reception of its predecessor. A review of the first edition was published in Volume 35 (p. 352, 1950) of this *Journal*. This edition is essentially the same as the first edition except for the following minor changes:

Page 4: Fig. 5 is new.

Page 16: Old Fig. 26 is deleted, old Fig. 27 is now Fig. 26.

Page 17: A new figure of a two-circle goniometer has been added as Fig. 27.

Page 92: A short paragraph has been added on the fundamental circle (ground circle) in the gnomonic projection and figure 166 has been modified by the addition of this circle.

Page 258: The following has been added to the last line on the page "... and these symbols are to be preferred (see page 273)."

Page 268: Added to the end of line 13, "(see p. 273)."

Page 271: The last four lines at the bottom, p. 272, and the top 10 lines on page 273 are all new.

The major change in this book is the addition of a 21 page chapter entitled "Diffraction of X-Rays by Crystals" which is a brief but well presented and well illustrated treatment of this subject. It will serve as a real help to the student in making the transition from crystallography to x-ray crystallography.

This edition should prove equally as popular with students as did the first edition.

GEORGE T. FAUST

THE EVOLUTION OF THE IGNEOUS ROCKS. By NORMAN L. BOWEN, pp. 334 plus 8, 82 illustrations, "Dover Edition," Dover Publications, Inc., New York, 1956. Price \$3.75, cloth bound; \$1.85, paper covers.

The "Dover Edition" of this treatise contains the entire text and illustrations of the first edition published by the Princeton University Press. The introduction to this new edition is written by Bowen's colleague, Dr. J. F. Schairer. He has added a bibliography (8 pages) of the papers by N. L. Bowen complete to 1954.

This is a classic work, available at a reasonable price. It should be in the library of every student of earth sciences who is interested in the origin and diversity of igneous rocks and of their tectonic significance.

GEORGE T. FAUST

**BAU UND BILDUNG DER KRISTALLE. DIE ARCHITEKTONIK DER STOFF-
LICHEN WELT.** By FRANZ RAAZ AND ALEXANDER KÖHLER, pp. 185, 166 illustrations.
Springer-Verlag, Molkerbastei 5, Vienna 1, Austria, 1953. Price bound \$4.30.

Professors Raaz and Köhler prepared this volume of topical essays on the results of modern mineralogical research because they believe this information is of general interest to scientists and engineers.

Chapters I through XII are discussions of crystallography which present the laws of crystallography, symbolism, symmetry, crystal structure, x-ray studies, and chemical crystallography. Emphasis is placed on the vectorial character of the physical properties.

The second half of the book consists of fourteen chapters, averaging about seven pages each. The subjects discussed are the formation of minerals in nature, mineral synthesis, growth and habit of crystals, twin formation, gems and gem materials, play of colors in minerals (iridescent and aventurine minerals), luminescent minerals as guides to discovery of trace elements, the various concepts of the earth's interior, occurrence of gold and platinum, occurrence of iron, meteorites, methods of determining minerals, the laboratory of the mineralogist and petrographer, and finally, symmetry as a basic element of scientific knowledge.

The illustrations are generally of excellent quality. An atmosphere of informality is created by the inclusion of poetic selections and a reproduction of Albrecht Dürer's famous picture, "Melancholia."

GEORGE T. FAUST

CRYSTALLOGRAPHIC DATA FOR THE CALCIUM SILICATES. By L. HELLER AND H. F. W. TAYLOR. vi+79 pages, published for Building Research Station, Department of Scientific and Industrial Research, by Her Majesty's Stationery Office, London, 1956. Price (bound) 10s. 6d.

Uncertainty has long prevailed as to the identity and stability of many of the minerals and artificial crystalline phases reported in the system $\text{CaO-SiO}_2\text{-H}_2\text{O}$. Recently some progress has been made in clearing up the confusion. This progress has been largely due to work by the authors of this book, begun nearly ten years ago as part of a project under the direction of Professor J. D. Bernal at Birkbeck College, London. Dr. Heller is now at the Standards Institution of Israel, Tel Aviv and Dr. Taylor is in the Department of Chemistry, University of Aberdeen. Their report covers not only their own work but summarizes all modern work in the field.

The book contains descriptions of 10 anhydrous phases, 7 known as minerals, and 19 hydrous phases, 12 known as minerals, plus reference to several uncertain phases and mixed materials. Each description includes information on composition, natural occurrence, technical occurrence, synthesis, appearance, optical properties, density, unit-cell and a number of other items such as synonyms and relations to other phases, gathered under the heading "additional notes." All of the information is documented, there being a separate list of references with each description. In the section on anhydrous compounds 8 powder diffraction patterns are tabulated, 6 of them indexed, and in the section on hydrated compounds 22 powder diffraction patterns are tabulated, 12 of them indexed. Two appendices deal with "thermal dehydration" and "classification and structures" of the hydrated calcium silicates. A third appendix lists the 3 strongest lines in the powder x-ray diagrams of 29 phases in "A.S.T.M. arrangement."

It is pleasure to see a summary of a complex group of minerals well presented by those best qualified to deal with the subject by virtue of their own important contributions to it. The book is heartily recommended to mineralogists and to all who have to deal with calcium silicates.

A. PABST

University of California, Berkeley 4, California

THEOPHRASTUS ON STONES by EARLE R. CALEY AND JOHN F. C. RICHARDS; ix+238 pages; The Ohio State University, Columbus, 1956, \$6.00. (Contributions in Physical Sciences, No. 1, Graduate School Monographs.)

This volume consists essentially of the Greek text, the authors' translation, and detailed comments on the treatise "On Stones" by Theophrastus (372-287 B.C.). Also included are helpful prefatory materials, many references throughout the commentary, and both Greek and English indexes. It was prepared from three Vatican manuscripts and several other translations by a chemist (E.R.C.) at Ohio State University and a classicist (J.F.C.R.) at Columbia University. This work represents the only English translation since the second edition (1774) by John Hill, the original edition of which appeared in 1746.

In order to obtain such a translation many conjectural devices must be employed, and these are necessarily based on incomplete data on physical and chemical characteristics, designated localities and modes of occurrence, and described uses. Obviously differences of opinion are certain to arise, and many of them may never be fully reconciled. The authors conclude, for example, that a variety of Samian earth is probably kaolinite despite Theophrastus' statement that it is used mainly or solely for clothes. Inasmuch as the detergent properties of other clay minerals are much greater than those of kaolinite, this reviewer believes that this particular type of Samian earth probably contained appreciable quantities of montmorillonite or a hydromica.

"Many of Theophrastus' conclusions are surprisingly accurate. . . . Pliny obtained many facts and some myths from Theophrastus . . ." according to Ball (1950). Although we may accept this general statement without reservation, it cannot be assumed that Pliny always correctly interpreted Theophrastus. For example, straightforward correlation between their Greek and Latin names is not possible. *Adamas* of Theophrastus is usually corundum (including emery) according to the authors, because "it is very doubtful whether diamonds were ever known to the peoples of the Mediterranean region in ancient times." Ball concludes that Pliny's six sorts of *adamas* included diamond, quartz (rock crystal) and magnetite, but probably not emery (p. 242).

This work by Caley and Richards represents the latest attempt to interpret the writings of the earliest mineralogist and petrologist. It is a creditable contribution of linguistic and scientific value, and most reasonably priced.

DUNCAN McCONNELL

Ohio State University

BALL, SYDNEY H. (1950), A Roman Book on Precious Stones, *Gemological Institute of America, Los Angeles, Calif.*

VORRATSBERECHNUNG MINERALISCHER ROHSTOFFE by A. P. PROKOFJEV. German translation (from the Russian) by Oscar Oelsner and Ehrhart Peukert. 163 pp. 44 illustrations. VEB Verlag Technik, Berlin, 1956 (price not known).

This little volume could no doubt be of service to German readers in providing explicit directions for computing the tonnage and average content of metalliferous and nonmetalliferous deposits that had been developed by drill holes and/or underground

workings. For geologists familiar with the standard texts in English it offers little that is new in principle. From the list of references one might gather that all of the familiar methods of estimation were devised by Russian authorities mainly since 1930; if the author is acquainted with any of the voluminous British and American literature of the past 60 years, he has chosen to ignore it.

Perhaps the most enlightening topic is the manner of fixing the cut-off grade, i.e. the dividing line between minable ore and non-economic mineralization, an ever-perplexing problem that can be solved under conditions of a free economy only by an educated guess as to future metal prices and operating costs. In Russia, the engineer is apparently relieved of the duty of crystal-gazing by the Ministries concerned, which accommodatingly specify the minimum minable grade for ore of any metal. Unfortunately, however, this specification is not final since it is subject to modification for "technisch-ökonomischen" factors. How to adjust for them is not explained. Ores containing two or more recoverable metals are left hanging in mid-air, for in the absence of open-market metal quotations the combined grade must be determined by the use of conversion factors which are not specified.

In favor of the book it may be said that it provides a thorough and detailed explanation of all of the common methods of ore estimation, expressing the author's preference for two methods: estimation block-by-block, particularly applicable to vein deposits, and estimation from cross sections (or horizontal sections), rather than by prisms, particularly in the case of deposits developed by drilling. Special attention is given to sources of error and factors for adjusting them. Commendable emphasis is placed on an understanding of geological conditions in attempting any rational estimate.

H. E. MCKINSTRY

Harvard University, Cambridge, Mass.

AURARIA: THE STORY OF A GEORGIA GOLD-MINING TOWN, by E. MERTON COULTER. x+149 pages, 7 black and white illustrations. The University of Georgia Press, Athens, 1956. Price, \$3.00.

Gold was discovered in Georgia in 1828, and the mining town of Auraria was founded in 1832 on a ridge between the Etowah and Chestatee Rivers. Auraria grew within a year into a settlement of 1,000 people, with perhaps 10,000 others living in the surrounding country. But its boom was short-lived, as the nearby town of Dahlonega, becoming the county seat of Lumpkin County and the site of a United States mint, soon outstripped Auraria in size and importance.

A newspaper, *The Western Herald*, was published in Auraria for nine months; and the discovery of a complete file of this paper made possible the present narrative. This little book has considerable historical value, as it outlines the problems connected with the translocation of the Cherokee Indians from Georgia, and describes the social life of an early and apparently law-abiding mining community. Further interest accrues from the presentation of current ideas regarding personal liberty, states' rights, and the encroaching powers of the Supreme Court.

This book has little information for geologists or mineralogists. The average commercial value of the alluvial gold, given as 90 cents per pennyweight, indicates that its fineness was in excess of 900. The Philadelphia mint receipts of \$1,763,900 from Georgia, representing about 85,000 ounces during the period 1828-1837, shows the magnitude of the early production of gold; and the Dahlonega mint receipts of \$6,115,569 for the period 1838-1861, is a measure of the later production of this region.

JOHN B. MERTIE, JR.

NOTES ON PUBLICATIONS RECENTLY RECEIVED

TSUBOI COMMEMORATIVE VOLUME. A collection of petrological, mineralogical, and geological papers published in 1955 in Tokyo, Japan, in celebration of Prof. Seitarô Tsuboi's 60th birthday (1953) by his pupils and colleagues. The commemorative volume consists of the following parts: foreword; review of Professor Tsuboi's career; a collection of 13 papers which have been published in *Journal of the Faculty of Science*, University of Tokyo, Sec. 2, Vol. 9, Part 2; together with 21 other papers published in other Japanese scientific journals. Most of these papers deal with mineralogical and petrological problems, although there are a few on paleontology, tectonics, stratigraphy, and volcanology. A memorable tribute and a very significant group of scientific contributions. Price and availability not indicated.

PROGRESS IN ECONOMIC GEOLOGY. Commemorative volume for Professor Takeo Katō. This is a volume of 581 pages+22+6, consisting of 83 papers on economic geology and mining geology; unfortunately, for the American geologist, entirely in Japanese. Only a table of contents in the rear is in English. The main subject headings for groups of papers include genetic relations of ore deposition to magmatic activity, pegmatite deposits, contact metasomatic deposits, hydrothermal deposits, sedimentary deposits, metamorphic deposits, relations of ore deposits to geologic structure, wall rock alteration, metallogenetic provinces and epochs, geologic thermometry, laboratory investigation of ores, descriptions of Japanese ore deposits, and mining geology. The volume concludes with a tribute to Professor Kato. No price or availability is indicated. Chairman for the committee is Professor Takeo Watanabe, whose address is Geological Survey of Japan, Hisamoto-cho 135, Kawasaki-shi, Kanagawa-ken, Japan.

CHEMICAL ANALYSES OF IGNEOUS ROCKS, METAMORPHIC ROCKS, AND MINERALS, 1931-1954, by EILEEN M. GUPPEY, with petrological descriptions by P. A. SABINE. Compiled from the records of the Geological Survey. *Memoirs of the Geological Survey of Great Britain*, 1956. Available through Her Majesty's Stationery Office, London. 10s.6d. net.

ADMINISTRATION REPORT OF THE GOVERNMENT MINERALOGIST FOR 1955, by L. J. D. FERNANDO. *Ceylon Administrative Reports*, 1955, Part 4, June 1956. Although primarily concerned with administrative matters, the report contains summaries of the geology of several areas in Ceylon. Price, 50 cents; postage, 20 cents. Purchasable at the Government Publications Bureau, Colombo, Ceylon.

CLAY MINERALS BULLETIN, Vol. 3, No. 15, Oct. 1956. 13 papers dealing primarily with the preparation and investigatory techniques of clay minerals. Price to non-members, 6/-, through Dr. R. M. S. Perrin, School of Agriculture, Univ. of Cambridge, Cambridge, England.

THE GEOLOGY OF NEW HAMPSHIRE, Part 2: *Bed Rock Geology*, by MARLAND P. BILLINGS. New Hampshire State Planning and Development Commission, 1956. An excellent summary of the bed rock geology of New Hampshire based to a large extent upon the work of Billings and his students. Includes an excellent map in color. Available through the New Hampshire State Planning and Development Commission, Concord, New Hampshire, at a cost of \$3.50. The map by itself is \$2.00 if sold separately.

E. WM. HEINRICH

NEW MINERAL NAMES

Birnessite

L. H. P. JONES AND ANGELA A. MILNE. Birnessite, a new manganese oxide mineral from Aberdeenshire, Scotland. *Mineralog. Mag.*, **31**, 283–288 (1956).

The mineral occurs cementing gravel in a pan 0.5 to 1.5 inches thick at a depth of about 12 feet at Birness, 20 miles north of Aberdeen. Analysis gave SiO_2 , 18.92, Al_2O_3 3.32, Fe_2O_3 2.88, TiO_2 0.28, MnO_2 54.24, MnO 4.66, CaO 1.65, Na_2O 2.17, H_2O^- 5.88, H_2O^+ 4.99, sum 98.99%. Grain counts showed the sample to contain quartz 20.0, clay 7.3, limonite 5.2, rutile 0.1, birnessite 67.4% by weight. Deducting the impurities indicated, the formula $(\text{Na}_{0.7}\text{Ca}_{0.3})\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$ is obtained. Spectrographic traces of As, Ba, Cr, Co, Cu, Ge, K, Li, Mg, Mo, Ni, P, Pb, Sr, and Zr were found.

Some of the grains showed well-defined facets. Hardness $1\frac{1}{2}$, G. 2.9, corrected for impurities 3.0. The crystals are nearly opaque, dark brown in transmitted light. They are faintly birefringent and give an indistinct uniaxial negative interference figure; the n_s vary, but are approximately ϵ 1.69, ω 1.73.

The x-ray pattern consists of 4 lines: (in Å) 7.27 s, 3.60 w, 2.44 m, and 1.412 m. The two inner lines disappear when the material is heated to 110° ; the other two remain even at 300° . This pattern corresponds to that of synthetic (and natural) material previously described by several authors as “ δ - MnO_2 ” and “manganous manganite,” both of which are now considered to be disordered forms of a distinct crystal phase.

DISCUSSION: Further study is needed. The low indices of refraction are surprising for material with $\text{Mn}:\text{O} = 1.90$.

MICHAEL FLEISCHER

Bobkovite

YU. V. KAZITSYN. A new mineral, aluminum-alkali opal, bobkovite. *Kristallografiya* (1955), No. 4, pp. 116–125; from an abstract by E. M. Bohnshtedt—*Kupletskaya in Zapiski Vses. Mineralog. Obshch.*, **85**, No. 3, p. 376 (1956).

The mineral has an opaline appearance. It is grayish-white, translucent on fresh fracture, with waxy luster. On drying, it cracks and becomes opaque and white. Analysis gave SiO_2 89.20, Al_2O_3 2.87, Fe_2O_3 0.54, CaO 0.37, MgO 0.26, K_2O 0.28, H_2O 3.24, loss on ignition 3.08, sum 99.84%. Neglecting H_2O and loss on ignition, this gives $(\text{K}, \text{Ca}, \text{Mg}, \text{Fe})_{0.5}(\text{Si}_{29}\text{Al})\text{O}_{60}$. The most intense x-ray lines correspond to 3.24, 2.021, 1.650, 1.047, 1.788 Å; these are indexed on a cubic cell with $a_0 = 12.12$ kX, with $Z = 40$. The structure differs from that of all other modifications of SiO_2 . It is changed on heating at 950° ; after $1\frac{1}{2}$ hours at 1350° , inverts to cristobalite.

G. 2.238 ± 0.008 . Under the microscope, very fine-grained, with slight birefringence (up to 0.004), n about 1.45–1.46. “Observed in the zone of hydrothermal and metasomatic transformation of old rocks of eastern U.S.S.R., in fissures and cavities of leached carbonates.”

The name is for the crystallographer N. A. Bobkov.

M. F.

Ginzburgites

F. V. CHUKHROV. Colloids in the Earth's crust. *Izd. Akad. Nauk S.S.S.R.* (1955), p. 598; from an abstract by E. M. Bohnshtedt—*Kupletskaya in Zapiski Vses. Mineralog. Obshch.*, **85**, No. 3, p. 382–383 (1956).

The name ginzburgites is applied to a group of minerals with the general empirical

formula $(\text{Al}, \text{Fe})_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$, with n generally above 2, the ratio Al:Fe variable, and the ratio $(\text{Al}, \text{Fe})_2\text{O}_3:\text{SiO}_2$ ranging from 1:1 to 1:2.5. Distinguished from kaolinite by containing Fe. The heating curve corresponds to that of halloysite. Has a higher capacity for adsorption of bases than halloysites or kaolinites. The extreme greenish members of the group represent hoeferites; other members of the group have been described under the names ferrihalloysite, faratsihite, and others.

The name is for I. I. Ginzburg.

DISCUSSION: One might reasonably have supposed that the time was long past when such useless names would be proposed, without even x-ray data to support them. Hoeferite and faratsihite have been identified as nontronite or mixtures containing nontronite.

M. F.

Shorsuite

N. T. VINNICHENKO. Shorsuite—a new mineral species of the alum group. *Trudy Mirdle—Asiatic Gos. Univ.* **63**, 19–22 (1955); from an abstract by E. M. Bohnstedt—*Kupletskaya in Zapiski Vses. Mineralog. Obshch.*, **85**, No. 3, p. 377 (1956).

Analysis by E. F. Kasyanova gave Al_2O_3 12.15, Fe_2O_3 1.01, FeO 4.28, MgO 2.09, Na_2O 0.70, SO_3 37.07, H_2O^- 28.60, H_2O^+ 13.46, SiO_2 0.72, CaO and K_2O not detected, sum 100.08%, corresponding to $(\text{Fe}, \text{Mg})\text{Al}_2(\text{SO}_4)_4 \cdot 19.6 \text{H}_2\text{O}$. The author indicates that the sample may have lost water during storage.

The mineral occurs in fibers up to 1 cm. long, luster silky, color grayish-white. Hardness low. Soluble in water, giving a solution with astringent taste. N_p 1.5025, N_g 1.5175, extinction inclined. In the burner flame, easily fusible with effervescence. Found in Middle Asia in the zone of oxidation of aluminous deposits.

The name is for the locality (not given in abstract).

DISCUSSION: The mineral corresponds in every detail except the slightly high indices of refraction to a member of the pickeringitë-halotrichite group.

M. F.

Eunicite

J. E. PAIVA HETTO. Eunicite—nova variedade de montmorillonóide necontrada nos melafiros de compostos da Serra de Botucatu. *Engenharia, mineria e metalurgia*, **22**, No. 128, p. 99 (1955); from an abstract by E. M. Bohnstedt—*Kupletskaya in Zapiska Vses. Mineralog. Obshch.*, **85**, No. 3, p. 382 (1956).

The name eunicite is given to a yellow-green to green product of decomposition of melaphyres from the Serra de Botucatu, Portugal. It has conchoidal fracture, and an agate-like texture, with color zoning. Two analyses gave SiO_2 42.00, 42.00; Al_2O_3 18.50, 23.20; Fe_2O_3 10.10, 7.10; FeO 0.28, 0.40; MgO 2.80, 3.40; CaO 0.25, 0.20; Na_2O 0.35, 0.31; K_2O 0.21, 0.21; TiO_2 0.10, 0.20; P_2O_5 0.03, 0.07; H_2O^- 15.50, 12.50; H_2O^+ 10.60, 10.50, MnO trace, trace; sum 100.72, 100.09%. The ratio $(\text{Fe}, \text{Al})_2\text{O}_3:\text{SiO}_2$ was 1:2.7 to 1:3.0 for 4 samples. The cation exchange capacity was 80 to 100 m.e.q. per 100 g. on material dried at 110°. It is indicated that the mineral differs in its thermal curve from other clay minerals.

DISCUSSION: Insufficient basis for a new name for a montmorillonite mineral.

M. F.

Nenadkevite

V. A. POLYKARPOVA. Nenadkevite—a new uranium silicate. *Atomnaya Energiya*, No. 3, 132–134 (1956).

The mineral occurs in very fine (0.05–0.001 mm) prismatic crystals. Color black, greenish-black, brown, to reddish-brown, orange, and yellowish; different colors are ob-

served in single samples. Luster vitreous to greasy. Sp. gr. 4.16–4.81 (black), 3.80–3.91 (brownish), 3.65–3.70 (yellow-orange). No cleavage, fracture flat conchoidal. Very brittle. Non-magnetic.

Transparent, usually isotropic, rarely has anisotropic patches. In transmitted light the dark varieties are bottle-green with N_m 1.716–1.781; light varieties are yellowish with N_m 1.618–1.635. Dark varieties were amorphous but when heated to 600° gave an x-ray pattern analogous to that given by the light material. The strongest lines are 2.90, 1.883, 4.65, 3.50, 2.18, and 1.746.

Six analyses are given, showing a highly variable composition. Five contain UO_3 38.50–66.10, the other contains UO_3 30.94, UO_2 21.72; SiO_2 10.60–20.25, PbO 6.37–11.7, CaO 4.04–8.30, MgO 0.7–11.08, rare earths 0.31–1.29%, H_2O 5.6–9.86%. The formula is given as $(U^{+4}, Y, Ce) U^{+6} (Ca, Mg, Pb)(SiO_3)_2(OH)_4 \cdot nH_2O$. It is considered to be a member of the thorite-uranothorite series and to differ from coffinite in the substitutions for uranium.

Nenadkevite was found "in the zone of sodium metasomatism of iron-uranium deposits, associated with brannerite, uraninite, albite, aegirine, alkali amphiboles, and magnetite." The locality is not given.

The name is for K. A. Nenadkevich.

DISCUSSION: An unnecessary name for what is probably a variety of coffinite. Should not be confused with nenadkevichite (*Am. Mineral.*, **40**, 1154 (1955)).

M. F.

Urgite

R. V. GETSEVA. Hydronasturan and urgite—new minerals of the group of hydrated uranium oxides. *Atomnaya Energiya*, No. **3**, 135–136 (1956) (in Russian).

The name urgite is given to a reddish-yellow to amber-yellow oxidation product of pitchblende. It is vitreous, hardness 2–3, sp. gr. for low-water varieties 4.17. Dense, no cleavage, fracture conchoidal. Under the microscope variable, in part isotropic with n up to 1.705, in part biaxial with N_g 1.669–1.680, N_p 1.647–1.657. Gives no x-ray powder pattern.

Partial microchemical analyses gave: reddish-yellow, UO_3 70.83, PbO 2.67, $Al_2O_3 + Fe_2O_3$ 4.23, SiO_2 3.92, H_2O 10.42%; amber-yellow, UO_3 71.09, PbO 2.90, $Al_2O_3 + Fe_2O_3$ 1.89, SiO_2 3.80, H_2O^- 7.95, H_2O^+ 6.14%. Spectrographic analysis showed the presence of Mg, Co, Bi, V, Cu, I, and Be (?).

The name is from uranium and gidrat (hydrate).

DISCUSSION: Should not have been named. May be a mixture ("gummite"). Dr. Clifford Frondel points out that the optical data for biaxial material are close to those of uranophane and the analysis shows SiO_2 .

M. F.

Hydronasturan

R. V. GETSEVA. Hydronasturan and urgite—new minerals of the group of hydrated uranium oxides. *Atomnaya Energiya*, No. **3**, 135–136 (1956) (in Russian).

The name hydronasturan is given to a partially oxidized pitchblende. Two partial microchemical analyses gave UO_2 22.2, UO_3 54.07, PbO 5.64, H_2O 5.71%, and UO_2 11.90, UO_3 63.00, PbO 5.78, H_2O^- 3.77, H_2O^+ 3.44%. This is formulated as $UO_2 \cdot k UO_3 \cdot nH_2O$, $k = 2.3\text{--}5$, $n = 3.9\text{--}9$. Color black to bottle-green in fine fragments. Luster vitreous. Brittle with conchoidal fracture. Hardness decreases with increasing UO_3 and H_2O from 3.8 to 3.1. Sp. gr. of highly hydrated material is 4.3. Under the microscope, isotropic, n 1.715–1.738.

Gives no x-ray pattern except rarely diffuse lines of the uraninite pattern. Loses water up to 300°, remaining amorphous, and yields crystalline U_3O_8 at 500°.

No locality is given.

DISCUSSION: The material should not have been given a name.

M. F.

Borgniezite

PIERRE DE BETHUNE AND ANDRE MEYER. Les carbonatites de la Lueshe (Kivu, Congo belge) *Compt. rend* **245**, 1132–1134 (1956).

The name borgniezite is given to a sodic amphibole, whose pleochroism is reminiscent of that of glaucophane and some arfvedsonites, but which is distinguished from these by its large extinction angle. No other data are given.

The name is for G. Borgniez, who discovered the carbonatite, adjacent to which the mineral occurs.

DISCUSSION: There is no excuse for burdening the literature with such names.

M. F.

Abernathyite

M. E. THOMPSON, BLANCHE INGRAM AND E. B. GROSS. *Am. Mineral.*, **41**, 82–90 (1956).

Osumilite

AKIHO MIYASHIRO. *Am. Mineral.*, **41**, 104–116 (1956). *Am. Mineral.*, **39**, 690 (1954).

Metatyuyamunitite

T. W. STERN, L. R. STIEFF, M. N. GIRHARD AND ROBERT MEYROWITZ. *Am. Mineral.*, **41**, 187–201 (1956).

Coffinite

L. R. STIEFF, T. W. STERN AND A. M. SHERWOOD. *Am. Mineral.*, **41**, 675–688 (1956).

Niocalite

E. H. NICKEL. *Am. Mineral.*, **41**, 785–786 (1956).

Gerstleyite

CLIFFORD FRONDEL AND VINCENT MORGAN. *Am. Mineral.*, **41**, 839–843 (1956).

Lesserite

C. FRONDEL, V. MORGAN AND J. T. L. WAUGH. *Am. Mineral.*, **41**, 927–928 (1956).

NEW DATA

Starkeyite

OLIVER R. GRAWE. *Am. Mineral.*, **41**, 662 (1956).

Professor Grawe points out that the mineral described by him in 1945 as being $FeSO_4 \cdot 4H_2O$ was actually $MgSO_4 \cdot 4H_2O$ and transfers the name starkeyite to the latter composition. The name leonhardtite was proposed for this mineral in 1952 by Berdesinski (see *Am. Mineral.*, **37**, 1072 (1952)) and has priority over starkeyite for this composition. However, since leonhardtite has been in use since 1843 for a variety of laumontite, it seems best to use starkeyite for $MgSO_4 \cdot 4H_2O$.

M. F.

DISCREDITED MINERALS

Offretite (=Phillipsite)

H. STRUNZ. Die Zeolithe Gmelinit, Chabasit, Levyn (Phakolith, Herschelit, Seebachit, Offretit). *Neues Jahrb. Mineral., Monatsh.*, 1956, 250-259.

Offretite was described by Gonnard in 1890 (Dana's System, 6th Ed., P. 1043) as a new mineral with a composition close to that of phillipsite, but hexagonal or rhombohedral. X-ray study of material from the type locality shows it to be identical with phillipsite.

M. F.

Cryphiolite = mixture

G. F. CLARINGBULL AND M. H. HEY. The nature of cryphiolite, *Mineralog. Mag.*, **31**, 346-347 (1956).

Cryphiolite was described in 1886 by Scacchi as a phosphate-fluoride of Ca and Mg. X-ray photographs of one of Scacchi's original crystals shows it to be a pseudomorph after wagnerite, now consisting of a mixture of apatite, sellaite, and a little wagnerite.

M. F.

Diderichite (=Rutherfordine)

CLIFFORD FRONDEL AND ROBERT MEYROWITZ. *Am. Mineral.*, **41**, 127-133 (1956).

M. F.

Vesbine (=Volborthite)

C. GUILLEMIN, Contribution à la minéralogie des arsénates, phosphates et vanadates de cuivre. II. Phosphates et vanadates de cuivre. *Bull. soc. franc. mineral et crist.*, **79**, 219-275 (1956).

Vesbine was described in 1879 by Scacchi as yellow incrustations on Vesuvian lavas. Analyses by Zambonini and Carobbi, *Am. Mineral.* **12**, 1-10 (1927) showed it to be a lead copper vanadate, probably mottramite. A new analysis and x-ray study show no lead; the x-ray pattern is that of volborthite, $\text{Cu}_3(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$, plus an admixture of vésigniéite.

M. F.